JPRS-UCH-92-005
14 MAY 1992
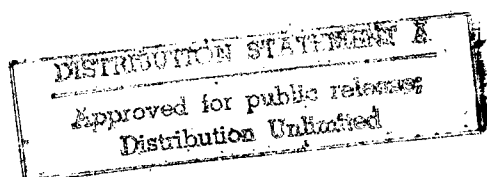
FOREIGN
BROADCAST
INFORMATION
SERVICE

JPRS Report

Science & Technology

Central Eurasia:
Chemistry

19980114 169

DTIC QUALITY INSPECTED 3

Science & Technology
CENTRAL EURASIA: Chemistry

CONTENTS

RADIATION CHEMISTRY

MISCELLANEOUS

AEROSOLS

Effect of Concentration of Aerosol Particles on Effectiveness of Their Deposition in Flow Thermodiffusion Chamber

[Article by S. P. Bakanov, V.V. Vysotskiy, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow; UDC 533.72:66.074.3]

[Abstract] Mathematical modelling and performance of a physical experiment were used to study diffusion and gravitational deposition of aerosol particles in a flow-thermodiffusion chamber with consideration of their condensation growth. Even at significant concentrations of aerosol particles, vapor condensation on them did not change the value of the vapor concentration gradient in the chamber and thus did not alter the effectiveness of the diffusion mechanism. The role of the condensation-gravitation mechanism decreased. Condensation of steam on the particles heated the gas and thus reduced the value of supersaturation. Figures 6; references 10 (Russian).

ANALYTICAL CHEMISTRY

Chelating Ion Exchangers With 3,5-Dimethylpyrazole Groups

[Article by Ye.Ye. Yergozhin (academician, KzSSR Academy of Sciences), K.N. Nurakhmetov, and B.A. Utkelov, Chemical Sciences Institute, KzSSR Academy of Sciences, Alma-Ata; UDC 541.183+547.77]

[Abstract] The main barriers to the wider-scale use of chelating ion exchangers are the labor-intensive multistage process required to produce them and their high cost. The use of costly polymer sorbents is most justified in the production and analysis of noble metals. But there is one major problem with using polymer sorbents together with noble metals. Sulfur-containing low-molecular reagents and polymers with sulfhydryl, thio-amine, thio ether, and dithiocarbamate groups form extremely strong bonds with gold and silver ions; however, they are unstable in redox media and hydrophobic, which creates significant problems when such sorbents are used in practice. In an effort to overcome these difficulties, the authors of the study reported herein synthesized and studied chelating ion exchangers with 3,5-dimethylpyrazole groups based on macroporous copolymers of styrene and divinylbenzene. The study ion exchanger was synthesized by reacting chloromethylated (26% chlorine) copolymers of styrene and divinyl-benzene (8%) with acetylacetone in the presence of sodium ethylate. The amount of bound acetylacetone groups was determined based on the residual content of chlorine in the polymer after the reaction. Studies of the effect of the ratio of starting reagents, concentration of sodium ethylate catalyst, and duration and temperature on the degree of copolymer transformation demonstrated that the highest content of acetylacetone groups is achieved when the reaction mixture is subjected to intensive stirring in an excess of acetylacetone at a temperature of 80°C for 10 hours with a copolymer-:acetylacetone molar ratio of 1.0:2.5 and catalyst concentration of 0.3 mole. The residual content of chlorine in the polymer amounted to 10%. To increase the hydrophilicity and improve the kinetic characteristics of the synthesized polymers, unsubstituted chloromethyl groups were modified by pyridine, cyanopyridine, picolines, pyridinecarboxylic acids, and selected aliphatic amines. The synthesis products were in the form of yellow-brown granules. Studies also established that copolymers with acetylacetone groups do not sorb copper, iron, and other transition metal ions, whereas low-molecular acetylacetone is a specific ion precipitator. To obtain a chelating sorbent, acetylacetone derivatives of the styrene + divinylbenzene (8%) copolymers were modified with hydrazine hydrochloride in the presence of an alkaline alcohol solution. The maximum amount of pyrazole cycles was found to form at 90°C for 6 hours with a copolymer:hydrazine molar ratio of 1.0:3.5. A comparative study of the kinetics of the sorption of gold from solutions with a starting concentration of 13 mg/l demonstrated that the synthesized polymer extracts up to 75% of the metal ions within 20 minutes, whereas the pyrazole sorbents used in analytic chemistry extract 50% of gold ions. Both types of pyrazole-containing ion exchanger were found to have a high chemical stability, and the reduction in their capacity for silver and gold ions after treatment by the respective acid, alkali, and oxidizer solutions did not exceed 5%. The new sorbents were determined to have more accessible complexing centers than do the familiar sorbents now used and thus a high chelation speed. Figures 4, table 1; references 14: 7 Russian, 7 Western.

CATALYSIS

Utilization of Spent Phosphoric Acid Catalysts

[Article by M. N. Rakhimov, Zh. F. Galimov, and R. M. Usmanov, Ufa Petroleum Institute; UDC66.095.264.3]

[Abstract] Spent phosphoric acid catalyst, used for polymerization of low molecular weight olefins, is one of the few petroleum refining catalysts not regenerated or reused elsewhere. Previous attempts at regeneration by oxidation of carbon deposits with air oxygen and steam proved unsuccessful. However, the annual volume of spent phosphoric acid catalyst comprises 400-450 tons of a commodity in short supply and that is a source of environmentally harmful hydrocarbon emissions. The rational for replacing spent catalyst lies in an unacceptably high reactor pressure drop owing to reduction in particle size, or a drop in olefin conversion rate. Spent catalyst, unloaded from a reactor, does not exceed 30-35 percent grain particles and contains as much as 20 percent adsorbed carbon. Research showed that the chemical composition of the catalyst changes somewhat during use and that the spent catalyst particles remain highly active, although low in mechanical strength, and for this reason cannot be recycled. In the present work it was demonstrated that fresh catalyst may be blended with up to 15 percent spent catalyst to provide a product that is sufficiently active and stable. Figure 1; references 4: 1 Russian, 2 Western.

Preparation of Aqueous Suspensions of Kaolin for Alumina- Silica Catalysts

[Article by A. V. Minibayev, R. M. Usmanov, R. N. Gimayev, N. Kh. Valitov, R. R. Zagidullin, and E. G. Fazlyyev, Bashkir State University imeni 40th Anniversary of the October Revolution; Ufa Petroleum Refinery; UDC 542.973]

[Abstract] The aluminum oxide content in the matrix of an alumina-silica cracking catalyst determines the stable activity of the catalyst. It may be raised from 9 to 18 percent or more by adding freshly precipitated aluminum hydroxide to the matrix together with kaolin clay resulting in higher strength, useful life, and less catalyst attrition. However, addition of kaolin has not yet entered domestic practice owing to the lack of developed methods for kaolin dispersal. In the present work a study of Kirovograd kaolin dispersal with a paddle mixer, laboratory blender, and ultrasonic disintegrator demonstrates that the latter method with 3 percent alkylaryl sulfonate yields a stable kaolin dispersion containing 86 percent particles of less than 4 microns. Figures 2; references 4: 3 Russian, 1 Western.

A Qualitative Study of the Relaxation Processes Occurring in a Two-Stage Heterogeneous Catalytic Reaction. Relaxation Time

[Article by A.G. Zyskin, F.S. Shub, and Yu.S. Snagovskiy, Physicochemical Scientific Research Institute imeni L.Ya. Karpov, Moscow; UDC 541.128.13:539. 196.3:541.127:519.6]

[Abstract] The authors of the study reported herein proposed a method of estimating the differences between the integral relaxation times of the rates of a two-stage heterogeneous catalytic reaction and the integral rate relaxation times obtained in a quasi-stationary approximation. They also proposed a method for determining the differences between the integral relaxation time of a coating and the coating relaxation times obtained in an approximation of linearization. They illustrate their theoretical analysis by way of sample calculations and present a table comparing the different methods of calculating reaction times for the two-stage reaction entailing the following two-way reactions: A + Z results in/from AI + D and B + ZI results in/from Z + C. The conditions of the proximity of the two methods were then analyzed. Results derived by using the two different methods were found to be closer to one another as the values of ε and the jump (i.e., the difference between the "old" and "new" stationary coatings) diminished. The authors concluded by cautioning that they have provided top estimates of the relative deviations in relaxation time and that the estimates presented may be somewhat elevated. Table 1; references 7 (Russian).

The Effect of Deuteration of the Solvent on the Process of Catalytic Oxidation of n-Xylene and the Conjugate Decarboxylation of Acetic Acid

[Article by N.G. Ariko, Physical and Organic Chemistry Institute, BSSR Academy of Sciences, Minsk; UDC 541.128.3:541.124-145.4:542.943:547. 534.2'023: 546.73'141-44]

[Abstract] The effect of deuteron substitution in a solvent molecule on the rate of oxygen absorption and carbon dioxide release was studied in an effort to refine the mechanism of acetic acid transformation during the course of catalytic oxidation of n-xylene. n-Xylene was oxidized under atmospheric pressure at a temperature of 368 K. Cobalt acetate tetrahydrate (CoAc$_2$) was used as the catalyst, sodium bromide was used as the promoter, and acetic acid was used as the solvent. Commercial

deuterium-substituted acids (CH$_3$COOD and CD$_3$COOD) were used. PMR spectroscopy indicated that the CH$_3$COOD had a deuterium content of 89.8% while the CD$_3$COOD had deuterium content of 94.5 and 81.4% in the carboxyl and methyl groups, respectively. The oxidation reaction was conducted in a circulation pressure gauge unit that permitted simultaneous determination of oxygen absorption and carbon dioxide release. The experiments conducted indicated that the kinetics of oxygen absorption and carbon dioxide release depend on the process' concentration parameters. When [CoAc$_2$]/[RH] $\geq$ 0.025 (Br$^-$/Co^{2+} = 2), the oxidation component of the process reaches its maximum speed after a period of rapid acceleration (lasting 2 to 8 minutes) and then remains constant until about 1 mole of oxygen per mole of hydrocarbon is absorbed. Under such conditions, the rate of decarboxylation increases gradually at first and then sharply toward the end of the period. When [CoAc$_2$]/[RH] < 0.025, the reaction develops more slowly. The maximum oxidation rate is reached almost simultaneously with the maximum decarboxylation rate. A sharp intensification of CO$_2$ release in the system is observed during the period of n-toluene aldehyde consumption and transition of Co^{2+} into Co^{3+}. The results are taken as an indication that decarboxylation of acetic acid under the study conditions cannot be explained within the framework of a mechanism including the formation of a carboxylate radical under the effect of peroxide radicals. Acetic acid is determined to be the source of carbon dioxide in all stages of the oxidation of n-xylene, although the extent of its participation in the decarboxylation process changes during the course of the reaction. Deuteration of acetic acid at its carboxyl group (a kinetic isotope effect [KIE] > 1) affects the rate at which n-xylene is oxidized, whereas deuteration of its methyl group (KIE < 1) mainly affects the rate of decarboxylation of the acetic acid itself. After a brief discussion of the question of the form in which the catalyst reacts with acetic acid, the author hypothesizes that transformation of acetic acid most likely occurs under the effect of the monobromide. Tables 2; references 12: 11 Russian, 1 Western.

Catalysis of the Radical Decay of Cumene Hydroperoxide by Secondary Aromatic Amines

[Article by L.N. Denisova and V.T. Varlamov, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Chernogolovka; UDC 541.128.12:541. 127:542.924:547.535-39:541.515: 547.554]

[Abstract] The authors of the study reported herein examined the catalysis of the radical decay of cumene hydroperoxide by secondary aromatic amines. Cumene hydroperoxide was reacted with eight different aromatic amines and N,N'-diphenyl-n-phenylenediamine, which is a vigorous acceptor of peroxide and amine radicals. The reaction was performed at 372 and 403 K (+/-0.5 K)

in a sparger-type reactor. The thermal expansion of the solvent (10%/100 K) was taken into consideration when the concentrations of the various reaction components were calculated. A method based on the phenomenon of catalysis is proposed for use in making a quantitative study of the reaction of aromatic amines with cumene hydroperoxide. According to the proposed method, aromatic amine acts solely as a participant in the study reactions whereas N,N'-diphenyl-n-phenylenediamine acts solely as an acceptor of the radicals formed in the reaction system. Because other existing methods determine k$_1$ (the effective constant of the rate of radical generation during pseudo-molecular decay of ROOH), those methods treat aromatic amines as fulfilling both the function of a participant in the primary reaction and a radical acceptor. The new method proposed herein is universal because the determination of k$_1$ is based on the rate of accumulation of one and the same substance, namely, QDI, which is the main product resulting when an aromatic amine is added to the system cumene hydroperoxide + N,N'-diphenyl-n-phenylenediamine. The new method has a much higher sensitivity than previously proposed methods: the value of υ_Σ may be determined reliably when [QDI] $\approx$ 10^{-5} mol/l. At aromatic amine [AmH] and ROOH concentrations of about 10^{-2} mol/l, this corresponds to a reaction depth of <1%. Even if the ROOH becomes involved in chain processes during the course of the reaction, the change in [ROOH]$_0$ during the course of an experiment will be negligible. Adding an aromatic amine to the system cumene hydroperoxide + N,N'-diphenyl-n-phenylenediamine will change the composition of the stable products and will reduce the rate at which a primary RO radical reacts with hydrocarbon (in the case described here with n-decane, k $\approx$ 10^9/l/mol/s and [AmH]$_0$ $\approx$ 10^{-2} mol/l). Adding aromatic amines thus protects the hydrocarbon from reacting with the primary RO radicals and reduces the rate at which its transformation products accumulate. Figures 4, table 1; references 19: 17 Russian, 2 Western.

Catalyst Activity in the Disproportionation of Methanethiol

[Article by A.V. Mashkina, V.R. Grunvald, B.P. Borodin, V.I. Nasteka, V.N. Yakovleva, and L.N. Khayrulina, Catalysis Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk; UDC 541.128.3: 542.924:542.973:541.183:547.269]

[Abstract] Under the effect of γ-Al$_2$O$_3$ at 370 and 410°, methanethiol is capable of decomposing into dimethyl sulfide and H$_2$S with a yield that is close to the thermodynamically possible yield. Dimethyl sulfide has also been observed to form when methanethiol decomposes on Al, Cr, Fe, Pd, and Ni metal and oxide films at 67 to 127° with a long contact time. Because such reactions have yet to be researched in detail, the authors of the

study reported herein examined the effect of catalyst activity on the disproportionation of methanethiol on various catalysts. The methanethiol used in the experience was obtained by using alkali to decompose methylisothiourea sulfate. The disproportionation experiments were performed in a continuous reactor, and the reaction products were subjected to chromatographic analysis under atmospheric pressure. The experiments lasted between 30 and 60 minutes. The technique of passing helium through methanol located in a thermostatted sparger was used to feed the methanol into the reactor. The different catalysts' activity was estimated based on the total rate of methanethiol conversion (r, mmol/h) per 1 g ("weight" activity) or 1 m^2 ("specific" activity). Twenty-five catalysts were tested. Regardless of the individual catalyst tested, the depth of methanethiol transformation increased as the reaction temperature increased. When the temperature and methanethiol concentration were kept constant, the yield of dimethyl sulfide increased as τ increased. In the case of most of the catalysts tested at 200 to 500°, no destruction of methanethiol with elimination of the hydrocarbon was observed, and selectivity with respect to dimethyl sulfide equaled 100% even at an equilibrium depth of methanethiol conversion. When τ was large, release of methane was observed in addition to the formation of dimethyl sulfide, with the methane yield increasing as contact time increased. In the presence of some of the study catalysts (SiO_2, HNaY, NaX, AlSi, MgO, and Cr_2O_3), disproportionation of methanethiol to dimethyl sulfide and H_2S was accompanied by the release of methane at low temperatures and far from equilibrium. SiO_2 showed the lowest level of activity. Its activity increased when it was modified with acids or when AlSi or HNaY was used, thus pointing to the participation of Bronsted acid centers in the reaction. The high-silica zeolite HZSM-5 was found to have both a high weight and a high specific activity that far exceeded the activity of the aforesaid catalysts (specifically, it had an activity of 2,000 µmol/h as referenced to one Bronsted acid center). The researchers hypothesized that the disproportionation of methanethiol on HZSM-5 involves not only Bronsted acid centers but base and Lewis acid centers as well. The need for a catalyst of the disproportionation of methanethiol to have base centers as well as acid centers was confirmed by comparing the activity of Al_2O_3 with and without additives of the said catalyst modified by acid oxides (Cr_2O_3, MoO_3, and WO_3) and acids (HF, H_2SO_4, HCl). The rate of methanethiol disproportionation on modified catalysts was less than on the starting γ-Al_2O_3. The experiments further revealed that combining base centers with strong Bronsted acid centers is likely less advantageous than is combining a base center with a strong Lewis acid center. Figures 2, tables 3; references 11: 8 Russian, 3 Western.

Mechanisms of Heterogeneous Catalytic Reactions of Organic Sulfur Compound Synthesis

[Article by A.V. Mashkina; UDC 541.128.541. 124:546.221-44:542.941.7'924: [547.73+547.279]]

[Abstract] Because of the long-prevailing view that sulfur-containing substances were highly contaminating to catalysts of processes involving non-sulfur-containing compounds, the catalytic synthesis of organic sulfur compounds was largely ignored by researchers. Techniques of deactivating catalysts subjected to the effect of sulfur compounds do exist, however, and chemisorption lies at the foundation of most of them. The suitability of conventional catalysts for use in synthesizing organic sulfur compounds depends primary on their stability during the synthesis process. Metal catalysts have been demonstrated to remain stable primarily in low-temperature processes of partial oxidation and in selected heterolytic reactions. In high-temperature processes occurring in an inert medium or in the presence of H_2 only sulfide catalysts retain their stability. Catalysts may be effectively used in several types of organic sulfur compound synthesis reactions. Hydrogenation of unsaturated sulfones by means of metal catalysts is possible. The mechanism of the said reaction is analogous to that established for liquid-phase hydrogenation of olefin compounds on transition metals capable of activating both the olefin bond and H_2. In the hydrogenation of unsaturated sulfones, the following metals may serve as catalysts (ranked in order of decreasing specific activity): Rh > Pd > Pt > Ir > Ru > Ni. Group VIII metals may be used in the hydrogenation of thiophenes, but their activity level is extremely low. Palladium sulfide applied to the carrier permits hydrogenation of the thiophene ring with a selectivity of 90 to 97%, a conversion up to 50%, and a catalyst productivity of 200 g thiophene/g catalyst/h, and its activity and stability are three orders of magnitude higher than those of metallic Pd. In the area of catalytic oxidation of sulfides, transition metal oxides may be used successfully as catalysts of partial oxidation reactions, and sulfates or sulfonates may be used as catalysts of deep oxidation. Cyclization reactions represent another area in which heterogeneous catalysts may be used to synthesize organic sulfur compounds. Thiols, disulfides, and aliphatic and cyclic sulfides and their oxides are dissociatively chemisorbed on catalyst surfaces at elevated temperatures. The hydrocarbon fragments formed undergo various transformations, including dehydrogenation to -CH-CH groups that may in turn be condensed with the sulfur atoms on the surface to form thiophenes. Sulfide synthesis is another area in which heterogeneous catalysts may be used. Specifically, one method of producing dialkylsulfides is through the disproportionation of alkanethiols, with Al_2O_3 being a particularly important catalyst in this area. Figures 3, tables 2; references 44: 35 Russian, 9 Western.

The Catalytic Properties of Oxides of Group III Elements Applied to MgO in the Reaction of the Oxidizing Condensation of Methane

[Article by M.Yu. Sinev, Yu.P. Tyulenin, and B.V. Rozentuller, Chemical Physics Institute imeni N.N.

Semenov, USSR Academy of Sciences, Moscow; UDC 541.128.3:542.953'943.7:547.211:546.6'46-31]

[Abstract] The authors of the study reported herein examined the catalytic properties of group III element oxides applied onto MgO in the oxidizing condensation of methane. The catalysts were prepared by impregnating MgO with aqueous solutions of nitrates of group III metals and then drying them at 120° and roasting them for 3 hours at 850° in air. When the content of applied ions ranged from 10^{-3} to 3% (atomic) of the Mg^{2+} ions, the specimens were determined to have a specific surface of 15 m^2/g. Methane oxidation was studied in a continuous quartz reactor with a 1:1 ratio of the starting CH_4:air mixture. The method used in the experiment was as described elsewhere. The sensitivity of reaction product determination amounted to 0.001% (volume) with respect to C_2 and CO_2 and 0.005% (volume) with respect to CO. A Bruker ESP-300 spectrometer equipped with a cyrogenic attachment was used to record EPR spectra at a temperature of 19 +/- 2 K. The activity and selectivity of identical quantities (0.3% (atomic)) of the group III metal ion-containing catalysts tested varied greatly. The following general laws noted previously for a broad set of oxide catalysts of oxidizing methane condensation were also found to apply to the experiments conducted: 1) the parallel formation of products of the oxidizing condensation of methane and deep oxidation at low conversion rates; 2) an increase in selectivity with respect to C_2 hydrocarbons when the temperature increased to about 750°; and 3) the formation of ethane as the primary product of the oxidizing condensation of methane (the formation of ethylene was not established at ethane concentrations of <0.02% (volume) in the reaction mixture). The fact that these laws were at work led the authors to hypothesize that the process of oxidizing condensation of methane occurs in accordance with a heterogeneous-homogeneous mechanism involving the formation of methyl radicals when the methane molecules from the gaseous phase react with the oxidizing center. The experiments performed revealed that catalyst activity and selectivity generally decrease as the order number of the catalyst element within subgroups IIIa and IIIb or within the lanthanoid series increases. Overall, the slope of the curves indicating catalyst effectiveness was similar to that of the curves indicating the increase in ionic radius of the applied M^{3+} cation. An analogous correlation was observed in the series of alkaline earth oxides and alkaline metal oxides applied onto Al_2O_3. The activity of Nd/MgO was found to increase as the amount of applied neodymium and the temperature of preliminary roasting were increased. M_2O_3 crystallites that begin to form at surface concentrations as low as M^{3+} <1% and that are dispersed on the carrier surface were shown by EPR spectroscopy to be the active component of the catalysts. Figures 3, table 1; references 16: 10 Russian, 6 Western.

The Effect of Oxide Precursors on the Catalytic Properties of Copper-Chromium Catalysts of Cyclohexanol Dehydrogenation

[Article by V.Z. Fridman, Ye.D. Mikhalchenko, B.G. Tryasunov, A.V. Ziborov, and L.M. Plyasova, Kuzbass Polytechnic Institute, Kemerovo, and Catalysis Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk; UDC 541.128.3:541.18.02:539.26:542.941.8:546.76'56-31:547.593.211]

[Abstract] The authors of the study reported herein used the methods of roentgenography and x-ray photoelectron spectroscopy to examine the effect of oxide precursors on the catalytic properties of copper-chromium catalysts of cyclohexanol dehydrogenation. The copper-chromium catalysts were prepared by the method of wet mixing of $CuCO_3 \cdot Cu(OH)$ and CrO_3 followed by drying and roasting. Two series of catalysts with identical $CuO:Cr_2O_3$ component ratios but different roasting temperatures were prepared. The following $CuO:Cr_2O_3$ ratios (by mass) were used: 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100. The first series of catalysts were roasted at 350°, which resulted in formation of the catalyst $CuCrO_4$. The second series of catalysts were roasted at 500°, which resulted in the formation of $CuCr_2O_4$ catalysts. Before the experiments, all of the catalysts were reduced in a hydrogen stream while the temperature was gradually raised at a rate of 2 K/min to 250°. The specimens were held at this temperature for 3 hours. A Dron-0.5 diffractometer was used for x-ray phase analysis of the series 1 specimens, and an HTK-10-PAAR high-temperature x-ray camera mounted on a DSOOSIEMENS diffractometer was used to analyze the specimens in the second series. The studies performed established that those copper-chromium catalysts that contained $CuCr_2O_4$ in their initial state had a much higher activity and selectivity following reduction than did those catalysts that contained $CuCrO_4$ in their starting state. The authors hypothesized that this increase in activity is caused by stabilization by that portion of the copper that is located in the spinel and that the increase in selectivity that is linked to the reduction in rate of cyclohexanol condensation is caused by the increase in the degree of chromium reduction on the surface of the said systems. Figures 3, table 1; references 17: 8 Russian, 9 Western.

The Effect of Complexing on the Catalytic and Cocatalytic Activity of Carbamide in the Cyclotrimerization of Isocyanates

[Article by N.V. Kozak and Yu.N. Nizelskiy, High-Molecular Compounds Chemistry Institute, UkSSR

Academy of Sciences, Kiev; UDC 541.128.3:541.49: 542.952.1:547.491.3:547.233]

[Abstract] Cyclic trimerization of isocyanate groups is an effective method of grafting and modifying diisocyanate-based polymer materials. Urea formation is one of the side reactions that exerts a significant effect on the course of cyclotrimerization. Because the existing literature data on the role of urea in the cyclotrimerization process are extremely contradictory, the authors of the study reported herein used a semiempirical quantum chemical approach to analyze the possible reasons for the significant differences in the catalytic and cocatalytic activity of carbamide in isocyanate cyclotrimerization reactions. The analysis performed demonstrated that the complexing of carbamide with the basic reagent and catalyst has a significant effect on the cocatalytic activity of carbamide in the cyclotrimerization of isocyanates. Specifically, the analysis demonstrated that urea formation in the process of the cyclotrimerization of isocyanates may result in the following effects: 1) the occurrence of secondary catalytic centers that act in synergy with the starting catalytic system; 2) a significant increase in active center activity owing to the formation of hydrogen-bound complexes with part of the carbamide molecules; and 3) deactivation of the reaction's active centers owing to zwitterion + carbamide complexing with the participation of two hydrogen atoms of the carbamide. These processes in turn result in the appearance of a sum effect whose equilibrium may be reaction shifted far to one side or the other (i.e., from activation to inhibition) depending on the conditions of the individual experiment. Table 1; references 8: 7 Russian, 1 Western.

Isomerization and Carbonylation of Esters Catalyzed by Platinum Phosphide Complexes in the Presence of Lewis Acids

[Article by N.Yu. Kozitsyna and I.I. Moiseyev, General and Inorganic Chemistry Institute imeni N.S. Kurnakov, USSR Academy of Sciences, Moscow; UDC 541.128.3:541.124-145.15:542.952.1:547.291'261: 546.92'181.1]

[Abstract] The authors of the study reported herein examined the isomerization and carbonylation of esters catalyzed by platinum phosphide complexes in the presence of Lewis acids. Specifically, they worked to find catalysts that would make it possible to produce carboxyl acids and acid anhydrides from methanol ethers under soft conditions without using Rh or I. Methyl formate and methyl acetate were dried by using anhydrous $CaCl_2$ and then distilled in an Ar atmosphere over P_2O_5. The BF_3 was purified by double low-temperature vacuum distillation. $[PPh_2Pt]_n$ (I) was produced by using formic acid to reduce $[(OAc)_2PtPPh_3]_2$ (II). A quantity of 1 g

(8.7 x 10^{-3} moles) of complex 2 was placed in a double-neck flask, and 4 ml of absolute HCOOH was added in an Ar atmosphere. The contents of the flask were stirred until C_6H_6 was no longer released. The HCOOH was boiled off. The precipitate was dissolved in benzene and filtered. The mother liquor was boiled off, and complex I was precipitated. Analysis revealed 37.94% C and 4.63% H. The molecular weight of complex I was determined to be 3,783 equivalent units, which corresponds to $n = 10$. The catalytic reactions were conducted by adding the required amount of I and an oxygen-free ester to the flask, after which a calculated quantity of cocatalyst was added. The BF_3 was condensed by freezing. After the mixture was thawed, Ar was added until atmospheric pressure was reached. The specimens were subjected to chromatographic analysis. The experiments performed indicated that when the polynuclear platinum phosphide complex I is added to an RCOOR' solution containing acids of the type BF_3, SbF_5, and CF_3COOH, $C_2H_5OCF(CF_3)CF_2OC_2F_4SO_3H$, acts as a catalyst of the isomerization of methyl formate into acetic acid and the carbonylation of methyl acetate into acetic anhydride at temperatures between 20 to 25° at a pressure of 0.1 mPa (Ar or CO, respectively). Figures 2; references 9: 6 Russian, 3 Western.

Problems in the Chemical Physics of Heterogeneous Catalysis

[Article by O.V. Krylov, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Moscow; UDC 541.128.13]

[Abstract] Progress in the theory of heterogeneous catalysis in the last decade has been linked to the rapid development of new physical research methods and new theoretical-mathematical methods, including quantum chemistry and a qualitative theory of differential equations. Specifically, new research methods have been developed that make it possible to study reactions of heterogeneous catalysis in situ with a low time resolution. Mass spectrometry analysis has made it possible to measure reaction times of 0.1 to 1 s in a continuous mode at atmospheric pressure and reaction rates of 10^{-3} to 10^{-4} s in a continuous vacuum version. Unique sampling methods have been developed that make it possible to take samples at distances of less than 1 mm from the catalyst and to thus improve time resolution to $<10^{-3}$ s. A system of physical methods (including IR, UV, and Raman spectroscopy) for in situ study of the catalysis process has, for example, been developed at the Chemical Physics Institute of the USSR Academy of Sciences. Laser methods have made it possible to reduce measurement times even further. The highest sensitivity ($10^3/cm^3$) has been achieved with the method of multiphoton ionization, which has a time resolution of 10^{-8} to 10^{-9} s and a spectral resolution of $10^{-3}/cm$ and which has been used successfully to study the quantum state of

desorbed molecules. Another recently developed method of studying surfaces is second-harmonic laser spectroscopy, which has been used to study the kinetics of the adsorption of O_2 on Rh(111) and Si(111) and the kinetics of benzene dehydrogenation. The short-wave femtosecond range began to be used in 1989. EXAFS is another noteworthy development. A second area in which a great deal of progress has been made is the dynamics of the elementary act of catalysis, including processes of energy exchange and electron exchange during catalysis. The use of modern laser detection methods has, for example, made it possible to record changes in the oscillation and rotation energy of scattered and desorbed molecules. The phenomenon of the "cooling" of molecules following a catalytic reaction has been observed, and an explanation of its patterns of occurrence is in the initial stages. The use of low-power pulsed lasers appears most promising in studying the process of electron excitation of a solid and adsorbed molecules in the visible and UV ranges at low temperatures. A third area in which substantial progress has been made in recent years is the macrodynamics of the catalytic process. Specifically, new physical and mathematical research methods have resulted in significant advances in understanding the formation of dissipative structures, chain mechanisms, heterogeneous-homogeneous catalysis, and the role of multiphasicity in heterogeneous catalysis. On the microscopic level, new approaches to describing the dynamics of catalytic processes with consideration for the interaction of the reaction medium and the catalyst are being used. The said processes are being examined from the standpoints of the thermodynamics of irreversible processes and synergetics. The topic of three-dimensional phase transitions and their role in catalysis have perhaps been best developed. The extremely important problem of synchronizing self-sustained oscillations in catalysis remains far from resolved, however. References 245: 83 Russian, 162 Western.

Behavior of Burning Particles and Flame Velocity in Gas Suspensions

[Article by S. V. Goroshin, Yu. L. Shoshin, and A. N. Zolotko, Odessa State University imeni I. I. Mechnikov; UDC 536.46]

[Abstract] Mathematical modeling was used to study flame front characteristics in the transitional area from kinetic to diffusional behavior. The model consisted of four differential equations involving activation energy, heat capacity, particle radius, temperature, oxygen concentration, diffusion coefficient, heat effect, and the stoichiometric coefficient of the reaction. These equations described gas temperature change, particle temperature change at the flame front, transfer of gaseous oxidant in the flame and particle combustion. An iterative solution was found which gave the rate and structure of the stationary flame front as a function of excess oxidant and initial particle diameter r_0. Curves of combustion rate versus r_0 exhibited an anomalous region where the dependence was much weaker that the inverse square root of r_0. This anomaly was wider at nonstoichiometric concentrations and was due to the opposite effects of increasing reaction surface and heat loss. Abrupt shifts from diffusional to kinetic control were seen in the anomalous areas. In most real cases flames can not be maintained under kinetic control. In lean mixtures no abrupt shifts were seen. Figures 2, references 6: Russian.

Exciting Shock Waves When Rarefaction Waves Interact With a Region of Spontaneous Combustion in a Gaseous Mixture

[Article by S.P. Medvedev, A.N. Polenov, and B.Ye. Gelfand, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Moscow; UDC 533.6.011.72]

[Abstract] The authors of the study reported herein used a model system to examine the gas-dynamic effects of the interaction of a brief rarefaction disturbance with a region of spontaneous combustion arising when a gaseous mixture is burned in a closed space. The measurement method used is based on the familiar phenomenon of spontaneous combustion in a specified stage of the combustion of an adiabatically compressed mixture before the flame front, i.e., upon the transition from a frontal to a volumetric combustion mode. The experiments were conducted in a horizontally configured cylindrical explosion chamber with an inner diameter of 50 mm and a length of 140 mm with one end sealed to a container that also had a diameter of 50 mm but had a length of 15 mm. The two spaces were separated by a blowout diaphragm. Piezoelectric pressure transducers and ionization flame indicators were used to measure the parameters of the process occurring in the explosion chamber. A stoichiometric mixture of acetone vapors and nitrogen-diluted oxygen (with a nitrogen content of 40% by volume) at a pressure of 0.2 MPa was used as the model substance. An initial pressure (p_1) of 0.1 MPa was used in the test space. Combustion of the mixture resulted in an increase in the pressure in the explosion chamber. When a pressure (termed p_2) determined by the thickness of the diaphragm was reached, the diaphragm ruptured, and a brief rarefaction pulse was propagated along the explosion chamber. Because the reacting mixture was, for all practical purposes, kept inside the explosion chamber, the gas-dynamic effects caused by propagation of the rarefaction wave could be directly compared with the combustion characteristics determined inside the closed space. The minimum pressure $p_2 = p''$ at which interaction of the rarefaction wave with the region of spontaneous combustion is likely was estimated. The case of acceleration of the flame upon interaction with obstacles was also modeled in some of the experiments. The main result of the experiments conducted was that there are two modes of interaction between a rarefaction wave and the reacting medium. The first mode occurs when $p_0 < p_2 < p''$ and when $p' < p_2 < p_m$ (p_m being the maximum explosion pressure and p' being the actual pressure in the explosion chamber). When this mode is in play, despite the increase in the rate of pressure, the maximum pressure in the explosion chamber is slightly in excess of the explosion pressure; it is reached after 2 or 3 runs of the rarefaction pulse. The second mode is observed when $p'' < p_2 < p'$. In the latter case, the result of the "primary act" of interaction with the rarefaction wave is the occurrence of a strong shock wave. The local pressure in the explosion chamber is significantly greater than p_m. The experiments performed confirm that strong shock waves are excited when rarefaction waves interact with the region of spontaneous combustion of a gaseous mixture in a reaction space. The results obtained in the research reported here qualitatively conform to previously published calculations obtained within the framework of the concept of a "gradient" mechanism. The most dangerous mode from the standpoint of interaction of a rarefaction wave with a region of spontaneous combustion is that of ignition of the mixture far from the diaphragm zone. The gas-dynamic effects observed are very similar (both from the standpoints of external appearances and formation laws) to the widely known phenomenon of the occurrence of a "knock" in internal combustion engines. Consequently, the interaction of rarefaction waves with a region of spontaneous combustion may be one of the reasons for the sudden appearance of "knocks" during an engine's normal operation. Figures 2; references 7: 5 Russian, 2 Western.

Investigation of Fuel Combustion Reactions and
Catalysts. XI. The Effect of the Method Used To
Modify Aluminum Oxide on the Formation of
Low-Temperature Solid Solutions in
Aluminomagnesium Systems

[Article by N.A. Koryabkina, Z.R. Ismagilov, R.A.
Shkrabina, E.M. Moroz, and V.A. Ushakov, Catalysis
Institute, Siberian Department, USSR Academy of Sci-
ences, Novosibirsk; UDC 542.973:546.46'623-
36:541.12.01:539.4]

[Abstract] In a continuing investigation of fuel combus-
tion reactions and catalysts, the authors of the study
reported herein examined the effect that the method
used to modify aluminum oxide when forming low-
temperature solid solutions in aluminum-magnesium
systems has on the products formed. Spherical alu-
minum oxide carriers (granule diameter, 2 to 3 mm)
were prepared based on commercial hydroxide with a
pseudo-boehmite structure. The hydrocarbon-ammonia
method was used to form the granules. Two methods of
magnesium modification were used, namely, adding a
magnesium nitrate solution to spherical granules of
aluminum hydroxide and to γ-Al_2O_3. The magnesium
content in these specimens ranged from 2 to 8% (by
mass). The specimens were roasted at temperatures from
383 to 823 K. The modified specimens were compared
with unmodified control specimens of γ-Al_2O_3. The
x-ray and diffraction studies performed showed that
depending on the method used to add magnesium and
on the heat treatment temperature, three different types
of solid solutions with a γ-Al_2O_3 structure may form:
anionic, anionic-cationic, and cationic. The mechanical
strength of the spherical aluminum oxide specimens
produced was also found to depend on the modification
technique selected. The strongest specimens were
obtained when magnesium was added to aluminum
hydroxide followed by roasting at 820 K. The increased
strength of granules produced by the said technique was
attributed to the formation of mixed-type (anionic-
cationic) solid solutions given the specified Mg/Al and
anion ratio. Tables 2; references 11: 7 Russian, 4
Western.

New Data on Geochemistry of Natural Water of Urovskaya Endemia Region in Siberia

[Article by L. V. Zamana, and N. M. Gladkaya, Chitinskiy Institute for Natural Reservoirs, Siberian Department, USSR Academy of Sciences; UDC 550.4(571.55)]

[Abstract] Kaschin-Beck disease, also known as Urovskaya endemia, has been associated with a calcium defficiency accompanied by some excess strontium. Recently a new theory has been proposed for this disease, connected with phosphate-managnese intoxication. The hydrogeochemical studies reported in the present work covered more macro- and microelements, resulting in some additional features of natural water in the disease region which may have been previously overlooked. Elevated phosphorus levels in the water supply, as high as 1.65 mg/L, were accompanied by increased incidence of the disease. Elevated phosphorus levels have been noted in the serum and urine of Kaschin-Beck patients and experimental animals. While decreased calcium levels were seen in the water of disease foci, the Ca/P ratio was a much more important determinant. Phosphorus levels above 0.1 mg/L with Ca/P ratios below 300 can be considered predictive for increased disease incidence. The decreased incidence of the disease in villages situated on carbonate rocks is due to the increased Ca levels, and thus Ca/P ratios, in their water. Strontium levels were not different in disease foci, compared to other locations. A positive correlation was seen between managnese and inorganic phosphate levels. Silicon levels were also elevated in locations with increased disease incidence, while magnesium levels were depressed. The negative effects of these anomalies on phosphate-calcium metabolism are exacerbated by the widespread cobalt and iodine defficiencies in the water of the entire region. Elevated sodium, molybdinum, copper, and tin levels were observed in the water of disease foci; these elements have been implicated in various bone or joint diseases. Elevated fluoride levels were not correlated with disease foci. While lithium levels were depressed, the fluoride-lithium hypothsis was not confirmed. The results obtained should be noted by biogeochemists and physicians as possible complicating factors in Kaschin-Beck disease. References 11: Russian.

Optimization of Method for Obtaining Propargyl Alcohol

[Article by A. I. Moiseyev, V. K. Stankevich, G. K. Balakhchi, A. I. Mikhaleva, R. N. Nesterenko, and B. A. Trofimov, Associate Member, USSR Academy of Sciences, Irkutsk Institute of Organic Chemistry, Siberian Department, USSR Academy of Sciences; UDC 547.362.3]

[Abstract] Mathematical optimization was used to improve the yield of propargyl alcohol from paraform-aldehyde and acetylene, with a potassium hydroxide catalyst and dimethyl sulfoxide solvent. The four factors studied were temperature of 45 or 15 , reaction time of 4 hours or 1 hour, paraformaldehyde quantity of 0.2 moles or 0.05 moles, and mixing speed of 1000 rpm or 350 rpm. An equation for yield in terms of these four factors was constructed and the optimum determined mathematically. Optimum conditions, which produced a yield of 95%, were 15, 4 hour reaction time, 0.05 moles of paraformaldehyde, and 350 rpm mixing. Reaction product workup was dilution 1:2 with water and methylene chloride extraction. Analysis was by GC. References 6: 2 Russian, 4 Western.

Rate of Anode Process in Passive Region of Alloys in Amorphous and Crystalline State

[Article by V. V. Gerasimov, V. V. Gerasimova, and A. G. Samoylov, Associate Member, USSR Academy of Sciences, Scientific Research and Construction Institute of Energy Technology, Moscow; UDC 621.031.53]

[Abstract] The log of the ratio of the rate of the anode process (i) in the passive region for crystalline and amorphous iron alloys has been found experimentally to be about 1.5 (average of 14 experiments). A semi-theoretical explanation for this observation was derived using the equation expressing Δlog i in terms of heat of vaporization E and adsorption energy Q: Δlog i = (E + 0.25)Q at room temperature. The difference in Q between the amorphous and crystalline states was calculated to be 202.5 kJ/mole, while the E difference was 26.9 kJ/mole. This gives a Δlog i of about 1.7, which does not differ from 1.5 in a statistically significant manner. References 12: 11 Russian, 1 Western.

Morphology of Microdiamonds and Content of Sodium Impurities in Garnets and Potassium in Pyroxenes of Two Xenolite Eclogites from Kimberlite of "Udachnyy" Shafts (Yakutiya)

[Article by N. V. Sobolev, academician, I. T. Baku-menko, E. S. Yefimova, and N. P. Pokhilenko, Institute of Mineralogy and Petrography, Siberian Department, USSR Academy of Sciences, Novosibirsk; UDC 552.8:549.21:571.56]

[Abstract] In order to verify the presence of microdia-monds in xenolith eclogites from the Udachnyy shafts, samples were subjected to thermochemical decomposi-tion. Diamonds with dimensions of 30-500 μm were found in two samples, exclusively in pyroxene granules. Microdiamond morphology was studied with a scanning electron microscope. The microdiamonds were classified into four morphological types. The first type exhibited shallow surface depressions and grooves in octahedral crystal facets. The second type had more prevelant and complex depressions with labyrinthine overhanging layers and rough pseudorhombododecahedral facets. The third type was defined by its pseudocubooctahedral habitat, while the fourth had predominantly pseudocubic facets with a shallow honeycombed lamellar or polycentric structure. Morphology and crystal dimensions indicated development by antiskel-etal growth rather than dissolution and corrosion. The existence of Na_2O impurities in garnet and K_2O in pyroxene has been considered a signal that microdia-monds may be present. Stable decreased average potas-sium levels in pyroxene from diamond-containing eclo-gytes, compared to diamond pyroxenes, suggest that extraction of potassium occurs under subsolid condi-tions with elevated pressure. The fact that potassium inclusion levels are not depressed in the current samples indicates that they recrystallized at higher pressures than usual for diamond-containing eclogytes. Figures 2; refer-ences 15: 11 Russian, 4 Western.

Investigation of Strong-Field Phenomena in the Dielectric Spectroscopy of Polymer Semiconductors

[Article by N.V. Afanasyev, L.V. Mukhayeva, M.G. Voronkov (academician), T.I. Vakulskaya, and V.A. Lopyrev, Irkutsk Polytechnic Institute and Irkutsk Organic Chemistry Institute, Siberian Department, USSR Academy of Sciences; UDC 537.311+537.226]

[Abstract] In view of the important role that the non-linear effects of electron relaxation polarization play in molecular electronics, the authors of the study reported herein used the dispersion graph method to determine the values of the parameters of the dielectric spectra of polymer semiconductors in a strong electrical field. The existing model of the polarization of conducting molec-ular chains describes two effects, namely, the reduction of the region of dispersion of dielectric permittivity ε' and its displacement to the side of higher frequencies as the intensity of a variable electrical field E increases in accordance with experimental data for polyacenoquino-nes. It has not yet been possible, however, to derive field dependences of the parameters of the dispersion region

owing to the ambiguity of making a circular diagram in the case of the high specimen conduction that is observed in a strong field, and that makes it difficult to measure the loss coefficient ε" in the audio-frequency range. The method developed by the authors consists of combining the graphs of the experimental and theoretical frequency dependences of the relative dielectric constant ε_1 and loss coefficient ε_2 described by generalized Debye equations. Dispersion graphs were plotted for specimens of 76YeNYe polyacenoquinone on the basis of data published in three separate sources, and the differences between the results presented in each source were discussed. Next, the authors studied the dependence ε(E) for polymer ion-radical salts of tetracyanoquinonedimethane. They interpreted it on the basis of the concept of the polarization of conducting molecular chains by analogy with polyacenoquinones. By considering experimental data published by Ikeno, Matsumoto, Yokoyama, and Mikawa in 1977 as their primary data, the authors were able to determine the structure and values of the parameters of the dielectric spectra by using circular diagrams and dispersion graphs. They discovered three dispersion regions analogous to those observed in the spectra of polyacenoquinones. The first dispersion region, which may be explained in terms of interlayer polarization, is associated with the Schottky barrier that has only been detected in a complex salt. At a temperature of 299 K its parameters have the following values: $\Delta\varepsilon' = 5.6 \times 105$, $\varepsilon'_\infty = 100$, $v_m = 3.6$ kHz, and α = 1. The second dispersion region, which may be explained in terms of the electron relaxation polarization of the grains, has been detected in a simple salt. At a temperature of 299 K its parameters have the following values: $\Delta\varepsilon' = 80$, $\varepsilon'_\infty = 5.5$, $v_m = 50$ Hz, and α = 0.45. The third dispersion region, which may be explained by interlayer polarization of the grains, is observed only in this specimen at a temperature of 210 K and has the parameters $\Delta\varepsilon' = 2.3$, $\varepsilon'_\infty = 5$, $v_m = 2.5$ kHz, and α = 0.4. These findings were interpreted as a foundation for hypothesizing a wider-scale distribution of grains with respect to conduction than occurs in polyacenoquinones. The most significant nonlinear effects were expected in the first dispersion region, and comparatively weaker effects were anticipated in the third region. Figures 4, table 1; references 12: 7 Russian, 5 Western.

Thermodynamic Properties and Phase Stability in the System Y-Ba-Cu-O

[Article by G.F. Voronin, S.A. Degtyarev, and Yu.Ya. Skolis, Moscow State University imeni M.V. Lomonosov; UDC 541.11]

[Abstract] An experimental study was conducted to determine the thermodynamic functions of compounds and solutions of the yttrium superconductor system Y-Ba-Cu-O. The study compounds were produced by the solid-phase synthesis method. Barium was used in its oxide and peroxide forms and in the form of barium carbonate or nitrate. Both before and after the thermodynamic experiments conducted, the study specimens were subjected to roentgenography (with an FR-552 monochromator), differential scanning calorimetry, and thermogravimetry (with a Netzsch STA 409 calorimeter) studies. The iodometric titration method and an original method based on the dependence of the electromotive force of the Galvanic cell on the stoichiometry of the chemical reaction lying at the basis of the said cell's operation were used to determine the oxygen content in the phases. The electromotive force of each of the nine study chains was measured at several dozens of different temperatures in the interval from about 950 to 1,200 K. The measurements were subjected to statistical processing and the results summarized in a table. A model was then developed to describe the dependence of the thermodynamic properties of solid solutions of $YBA_2Cu_3O_{6+z}$ and $Y_2Ba_4Cu_7O_{14+z}$ on their oxygen content (z). Within the framework of the model, the formulas of the said phases are as follows. In the case of "123"-type semiconductors, $[X]^{-1} = (Y^{+3})_1(Ba^{+2})_2(Cu^{+2})_2(O^{-2})_6$; for "247"-type semiconductors, $[X]^{-1} = (Y^{+3})_2(Ba^{+2})_4(Cu^{+2})_5(Cu^{+3})_1(O^{-2})_{14}$. The model developed is said to uniquely describe the thermodynamic and structural distinctions of both crystalline modifications of a "123" phase. The numerical values presented were found by using 600 pieces of experimental data from 25 publications. The model is further said to adequately reflect all currently existing information about the thermodynamic properties of "123" phases. In addition to estimating the values of the thermodynamic functions of "123" and "247" phases, the researchers also used data published elsewhere to estimate the properties of $YBa_4Cu_3O_{8.5}$ phases. According to the calculations performed, a "123" phase is stable only in its tetragonal modification. Among the study compounds, "124" is the only one expected to remain thermodynamically stable under the conditions used. At low temperatures and close-to-atmospheric oxygen pressures, "247" should be transformed into "124." Figures 3, tables 3; references 15: 8 Russian, 7 Western.

Synthesis and Ion-Exchange Properties of Titanates. IV. Exchange Isotherms of Li⁺, Na⁺, Ag⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ Ions on Crystalline Potassium Titanate

[Article by L.P. Filina and F.A. Belinskaya; UDC 541.183.12]

[Abstract] Crystalline potassium titanate with the formula $K_{1.4}H_{0.6}Ti_4O_9\cdot1.5H_2O$ may be obtained from tetratitanic acid $H_2Ti_4O_9\cdot1.7H_2O$ by saturating it with potassium ions from a 0.1 N solution of KOH prepared

on the basis of 1 N KCl. This titanate possesses ion-exchange properties. The absorption of the ions Li^+, Na^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} on crystalline potassium titanate from a 0.1 N solution of salts was measured. A 1:100 ion-exchanger:solution volume ratio was used, and the specimens were kept in contact with the solution for at least 3 days with periodic stirring. A comparison of the absorption values obtained on crystalline potassium titanate with published data on the absorption of the said ions on x-ray amorphous potassium titanate indicates that the absorption of all of the said ions on the two forms of potassium titanate is close (and even virtually identical in the cases of silver, calcium, strontium, and barium ions). The isotherms of the said ions' exchange of crystalline potassium titanate were then plotted and analyzed. The isotherms were all complex in shape: They were all asymmetrical relative to the diagonal of the square. The selectivity of potassium titanate under the conditions studied was found to be as follows: $Ag^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. Selectivity with respect to Li^+ and Na^+ was found to depend on the molar fraction of sorbed ions in the solution: when $N_i < 0.5$, $Li^+ > Na^+$; when $N_i = 0.5$ to 0.8, $Na^+ > Li^+$; and when $N_i > 0.8$, $Na^+ \simeq Li^+$. The studies performed led to the hypothesis that the high specificity of potassium titanate with respect to alkaline earth metal and silver ions does not allow for the possibility of hydrolysis of the exchanger, whereas its hydrolysis in solutions of salts of other alkaline metals does take place, and the hydrogen ion that appears upon the hydrolytic splitting of the water is absorbed together with alkaline metal ions. This in turn led to the conclusion that cation exchange in aqueous solutions may, in certain cases, be looked upon as a ternary system of oppositely charged ions, i.e., two metal cations and hydrogen ions. The studies performed thus indicated that crystalline potassium titanate manifests high selectivity with respect to alkaline earth metal and silver ions but not with respect to ions of other alkaline metals. In this regard crystal potassium titanate is similar to x-ray amorphous potassium titanate. Figures 3; references 2 (Russian).

The Effect of the Adsorption of Nonionogenic Surfactants on the Stability of Natural Diamond Dispersions

[Article by V.M. Markovskiy and Ye.V. Golikova; UDC 541.18.046.61.185]

[Abstract] The authors of the study reported herein examined the effect of the adsorption of nonionogenic surfactants on the stability of dispersions of type AMO 0.5/0 natural diamond. As a nonionogenic surfactant, the authors used two commercial preparations based on polyethylene glycol ethers: arkopal [transliteration], i.e., a isononylphenyl ether of decaethylene glycol ($C_9H_{19}PhE_{10}$) and sintanol [transliteration] ALM-10 (i.e., $C_9H_{2n+1}E_{10}$ where n ranges from 14 to 12). The values of the critical concentration of micelle formation of arkopal and sintanol, as determined based on the change in surface tension, were found to be 3.5 x 10^{-4} and 6.0 x 10^{-4} mol/l, respectively. The adsorption of the study nonionogenic surfactants on the surface of the diamond particles (which averaged about 0.25 µm in size) was determined based on the difference between the equilibrium and starting concentrations of nonionogenic surfactant in the suspension, and the concentration of nonionogenic surfactant after centrifugation was found by a photometric method described elsewhere. The hydrophilicity of the modified diamond particle surface was estimated by a method of determining the coefficient of transfer of particles from the aqueous to the nonpolar phase. The said method is termed the philicity coefficient method and is based on the principle of oil flotation. The adsorption of nonionogenic surfactant was measured in the starting concentration interval from 10^{-5} to 10^{-3} mol/l for two background solutions, i.e., bidistilled water with a pH of 5.8 and with a pH of 2.0 (10^{-2} mol/l HCl). Adsorption was found to decrease as the pH increased, evidently indicating that the appearance of a charge in the particles impedes adsorption. This fact led the researchers to conclude that the adsorption of nonionogenic surfactants on natural diamond particles occurs primarily as a result of the formation of hydrogen bonds between the oxyethyl chains of the nonionogenic surfactant and the oxy groups of the surface. They further concluded that the structure of the hydrocarbon radical of the nonionogenic surfactant, given one and the same pH, has a marked effect on the extent of adsorption of both arkopal and sintanol. In view of the heterophilic nature of the surface of natural diamond, the researchers hypothesized that the interaction of the unoxidized (hydrophobic) sections of the surface with the hydrocarbon chains of the nonionogenic surfactant makes an important contribution to the process of arkopal adsorption on a natural diamond surface. They proceeded to conclude that it is perhaps more correct to assume that adsorption on an inhomogeneous surface occurs in both types of sections and that the predominance of one of the competing mechanisms (hydrophilic sections + an oxyethyl chain or hydrophobic sections + an aklyl chain) will determine the hydrophilic-lipophilic balance of the nonionogenic surfactant molecule. An increase in suspension stability at surfactant concentrations close to the critical concentration of micelle formation was discovered and attributed to two factors. The first was the hydrophilization of the surface (i.e., the structuralization of the water around the oxyethyl chains of the nonionogenic surfactant), and the second was the formation of a steric repulsion barrier. Figures 3; references 10: 7 Russian, 3 Western.

The Electronic Properties of Two-Dimensional Quantum Systems on the Surface of Narrow-Gap Semiconductors Close to Room Temperatures

[Article by A.D. Perepelkin and A.M. Yafyasov; UDC 621.315.592]

[Abstract] The authors of the study reported herein examined the electronic properties of two-dimensional quantum systems on the surface of narrow-gap semiconductors at temperatures approximating room temperature. Specifically, they conducted a theoretical investigation of the laws governing the change in the energy positions of quantum subbands E_i, the centroid of the total charge z_{av}, the incremental capacitance of the dimensionally quantized space-charge region C_{sc}, and other parameters of the space-charge region of narrow-gap semiconductors as a function of the effective mass of their heavy holes m^*_{hh} and temperature given a semiconductor with a fixed forbidden band width E_g, effective electron mass of m^*_e, and dielectric constant of ε_{sc}. The authors' analysis of the change in the parameters of the dimensionally quantized space-charge region of narrow-gap semiconductors was based on the self-consistent solution of Schrodinger and Poisson equations by using a numerical procedure proposed elsewhere. They focused their analysis on the narrow-gap semiconductors (CdHg)Te and (ZnHg)Te at temperatures between 250 and 300 K, inclusively. The calculations performed demonstrated that all of the parameters of the dimensionally quantized space-charge region of the two study narrow-gap semiconductors for the values of m^*_{hh} selected are qualitatively dependent on the surface potential v_s. The calculations and analysis performed led the authors to conclude that the model criterion of the onset of the filling of the two-dimensional quantum subbands makes it possible (albeit more qualitatively than quantitatively) to explain the general laws governing the behavior of two-dimensional systems as a function of surface potential (as well as temperature). They also concluded that both their analysis and analyses published elsewhere indicate that as the temperature decreases while v_s remains constant, the two-dimensional subband spectrum on the surface of a narrow-gap semiconductor changes in the same manner as when the surface potential increases while T = const. They explained this finding by the fact that the width of the semiconductor's space-charge region increases both when the temperature decreases and when the surface potential increases. The authors went on to state that the same may be said about the behavior of the other parameters of a two-dimensional system, such as incremental capacitance C_{sc}. Figures 4; references 6: 2 Russian, 4 Western.

Kinetics of the Process of Etching Porous Glass With an Alkaline Solution

[Article by O.M. Todes (deceased), T.M. Burkat, D.P. Dobychin, and V.M. Belugina, Leningrad State Pedagogical Institute imeni A.I. Gertsen; UDC 541.127:532.73:542.947:[541.454+549.691]]

[Abstract] The authors of the study reported herein examined the process of the etching of porous glass by an alkaline solution. Their primary objective in so doing was to gain a greater understanding of the macrokinetics of the dissolution of a solid in the internal kinetic region. First, a theoretical analysis of the said process was performed. The laws identified were then subjected to experimental verification. The verification experiments used porous glass disks 25 mm in diameter and 1 mm thick that had been produced by leaching disks of DV-1 sodium borosilicate glass in acid subjected to etching in alcohol. The initial pore radius was regulated by changing the temperature at which the specimens were heat-treated in the range from 585 to 715°C while keeping the treatment duration constant at 24 hours. The initial rates of increase in pore radius were found to increase as the initial pore radius increased in accordance with one of the equations derived by the authors during their theoretical analysis. Data obtained from the said experiments were used to calculate the reaction rate constant and diffusion coefficient; values of k = 0.67 angstroms/s and 6.8 x 10^{-6} cm^2/s were found. The study demonstrated that even during etching in the internal kinetic region, a decrease in the concentration of etching agent and etching rate by pore depth (plate thickness) is inevitable. Figures 3, table 1; references 15: 12 Russian, 3 Western.

New Type Diamond Deposit

[Article by L. D. Lavrova, Geological Prospecting Central SRI, Moscow]

[Abstract] For a long time it was believed that diamonds are formed only within the earth's mantle where kimberlite melts are formed at the theoretically necessary minimum temperatures and pressures of 1000° C and 40 kBar. However, in 1972 diamonds have been detected in ores comprising the Poligaysk meteorite crater which demonstrated that diamond crystals may be formed under the most diverse geological conditions and that diamonds originating from impactites are entirely different from those of kimberlites. The kimberlite diamonds are rather large sized colorless octahedral, rhombo-dodecahedral, or cubic crystals, while the impactite diamonds consist of a microscopic multitude of fine, cloudy, gray platelets. These and other special features of impactite diamonds evidently result from the

instantaneous crystallization under shock conditions of meteoritic impact where the temperature exceeded 1000-1200° C and the pressure also exceeded the minimum 40 kBar. Special methods, developed for separating these fine impactite diamonds, were applied to searching for diamonds in magmatic rocks such as basaltic peridotites and picrites considered to be of mantle origin. In 1967 fine diamond crystals were detected in sands from northern Kazakhstan which stimulated search for root source. Ten years later, in 1979, fine diamond crystals 0.02-0.07 mm were detected. Special properties and features of these diamonds are presented. It is postulated that in the future diamond formations may be discovered in otherwise unpromising regions. Figures 6; references 12 (Russian).

Phase Equilibria and Crystal Growth in Solid Ge-As-P Solutions

[Article by G.V. Semenova, I.I. Grekova, M.I. Kalyuzhnaya and Ye.G. Goncharov, Voronezh State University imeni Lenin's Komsomol; UDC 546.28'18+546.28'19]

[Abstract] Differential thermal analysis of phase equilibria of solid Ge-As-P solutions was carried out in order to determine optimum conditions for crystal growth. The phase diagrams facilitated estimation of stability parameters which were used in vapor-phase crystallization over a pressure range of 0.15 to 1.5 MPa. Samples of $GeAs_{1-x}P_x$ containing 27-68 mol% germanium phosphide were synthesized. A diagram relating crystal composition to melt composition for selected isotherms (990-1020 K) is provided. Figures 2; references 10: 9 Russian, 1 Western.

Electrophysical Properties of GaInAs Layers and Performance of Fast Photoresistors With Schottky Barrier Contacts

[Article by V.A. Vdovenkov, L.I. Kuzmina, V.M. Novikova, S.P. Prokofyeva, S.B. Stasenko and T.N. Usacheva, All-Union Scientific Research Institute of Optico-Physical Measurements; UDC 537.311.33:539.216.2]

[Abstract] GaInAs transducers were analyzed for responsiveness to 0.825 μm laser pulses as part of an assessment of the impact of electrophysical characteristics of GaInAs layers on performance of photoresistors with Schottky barrier contacts. Highest photoresponses (ca. 240-260 mWt) were obtained with p-GaInAs layers with high carrier mobility (ca. $10E4$ $cm^2/V.sec$)), low residual impurities (ca. $10E14$-$10E15$ cm^{-13}), and K = ca. 0.2

compensation. The sensitivity was on the order of 0.4 A/Wt, exceeding that of compensated GaAs and InP single crystal layers. Figures 2; tables 1; references 8: 4 Russian, 4 Western.

Heterogeneity Charge Carriers in Gallium Antimonide

[Article by Ye.S. Yurova, A.G. Milvidskaya, I.M. Yuryeva and G.P. Kolchina, 'GIREDMET' State Scientific Research and Planning Institute of the Rare Metals Industry; UDC546.681.3'863]

[Abstract] The requirements for a high degree of homogeneity in semiconductors led to an assessment of heterogeneity in electron distribution in p-GaSb in relation to crystal growth, crystal size and type and extent of doping (Te or Te+Si). The results demonstrated that [100] type crystal growth ensured maximum homogeneity which, however, was virtually unaffected by the type of dopants and crystal size within the 35-60 mm diameter range. Plots relating heterogeneity (δ) to electron concentration (n) in doped samples showed that $\sigma = < 15\%$ at n = > 5 x $10E+17^{-3}$. Figures 2; references 3 (Russian).

Superfast Tempering Method for Semiconductor Melts

[Article by V.M. Glazov, Yu.V. Yatmanov and Ye.M. Ryazanov, Moscow Institute of Electronic Technology; UDC 537.311.33]

[Abstract] Coverage is given to technical details on the operation and performance of a device for superfast tempering of semiconductor Bi-Sb melts, a process that yields semiconductors that differ markedly from coventional products. The resultant semiconductors consisted of 20-100 μm thick films, 5 to 120 mm long. X-ray spectroscopy of the $Bi_{0.9}Sb_{0.1}$ films demonstrated that cooling at a rate of $10E+7$ K/sec was a significant factor in reducing to a minimum heterogeneity in component distribution due to nonequilibrium crystallization of the melt. Figures 2; references 4 (Russian).

Formation of $YBa_2Cu_3O_{7-\sigma}$ Ceramics in Solar Furnace

[Article by V.B. Glushkova, S.Kh. Suleymanov, V.A. Krzhizhanovskaya, T.N. Baymatov, O.N. Yegorova and

Ya.Z. Yuldashev, Institute of Silicate Chemistry imeni I.V. Grebenshchikov, USSR Academy of Sciences; Physicotechnical Institute imeni S.V. Starodubtsev, Uzbek SSR Academy of Sciences; UDC 542.9]

[Abstract] Firing of a $YO_{1.5}$:$2BaCO_3$:$3CuO$ charge in a solar furnace at 1200-1500°C yielded $YBa_2Cu_3O_{7-\sigma}$ ceramics with orthorhombic structure after annealing at 945°C for 8 h and cooling at a rate of 100°C/h. The $YBa_2Cu_3O_{7-\sigma}$ has the following characteristics: density = 4.87 g/cm^3, cell parameters a = 3.818, b = 3.888 and c = 11.688 A, T_s = 92 K and critical I = 3.5 x 10^2 A/cm^2. Resistance at room temperature was on the order of 3 mOhm cm^{-1}. A key advantage of the process was the formation of intermediates that were less reactive with the walls of the container than BaO. Figures 5; references 6: 2 Russian, 4 Western.

Factual Database on the Physical Properties of High-Temperature Superconductors

[Article by A.M. Panich, L.I. Chernyavskiy, and M.V. Malkova, Inorganic Chemistry Institute, Siberian Department, USSR Academy of Sciences; UDC 538.945:681.3.06]

[Abstract] The significant disparity of data regarding the properties of high-temperature superconductors causes significant problems for researchers in the field. In an effort to remedy this problem, the authors of this concise report have proposed the creation of a factual database containing recommended and reference values for various properties of high-temperature superconductors. The database will include factual information designed to help users in three ways: 1) obtain information regarding the physical properties of high-temperature superconductors given specified external conditions (temperature, pressure, etc.); 2) select materials possessing a specified set of properties within a given range of external conditions; and 3) construct interrelationships and find correlations between various properties and parameters of high-temperature superconductors (including relationships and correlations that are not yet available in the scientific literature). Each document in the database will contain information about one feature of a specific substance of a specified composition and structure. The properties of monocrystals, ceramics, and films will be described separately. Also included is information regarding the method used to determine the values presented along with the reliability of the data and related bibliographic citations. The version of the new database that has been created includes a description of the magnetic properties of high-temperature superconductor and data on oscillation and radio spectroscopy in poly- and monocrystals. About 230 documents are included in the new database thus far. The database has been developed for use on IBM PC/AT's and is available in two versions, i.e., versions that can and cannot be expanded by the user. The new database will be provided without charge to organizations participating in the process of filling it.

The Chemistry of Processes of the Purposive Creation of Functional Dielectric Layers on Semiconductors During Their Impurity Thermooxidation

[Article by I.Ya. Mittova and V.R. Pshestanchik, Voronezh University; UDC 539.216.2:621.315.592]

[Abstract] Thin films are used in various areas of modern technology, including microelectronics, optoelectronics, and laser technology. Research devoted to the processes of the formation of thin films with diverse properties (including dielectric properties) on solid surfaces has greatly increased understanding of the kinetics and mechanism of heterogeneous solid-gas and solid-solid reactions. The chemistry of the processes of purposive creation of functional dielectric layers on semiconductors during impurity thermooxidation is especially important. Such research is based on a combination of formal kinetic studies and modern instrument-based physical and physicochemical methods that make it possible to unequivocally establish the composition of reaction products and to trace the distribution of components throughout a layer's thickness, identify changes in the composition and structure of layers and substrates, and thus obtain comprehensive information regarding the dependence of films' compositions on their formation conditions and on the kinetics and mechanisms of their reaction processes. Use of the methods of chemical etching and study of Faraday volt and dynamic volt-ampere characteristics have made it possible to establish the interconnection between the conditions under which dielectric layers and metal-insulator-semiconductor [MIS] structures are produced and their electrical characteristics. Research on the thermal oxidation of silicon and gallium arsenide has demonstrated that impurities have a significant effect on the kinetics and mechanism of the formation of dielectric oxide layers: They can accelerate the process, reduce the duration of the required high-temperature treatment, and alter the composition and properties of films within a broad range. The aforesaid research methods have also made it possible to discover the laws governing the processes of impurity thermooxidation of semiconductors induced by a class of dopants. Studies of the thermal oxidation of indium phosphide have revealed that it is the very mechanism of the formation of the dielectric layers themselves on InP that are responsible for their unsatisfactory properties. Dopants are required, first and foremost, to increase the efficiency of oxidation of indium both directly (transit dopant-indium) and indirectly by intensifying the oxidation of phosphorus (transit dopant-phosphorus) and attenuating its effect on In_2O_3. The system $In_2P_2O_5$ is actually more promising

than the system Ga_2O_3-As_2O_5 from a reaction standpoint because indium has better metallic properties than gallium and because phosphorus has better nonmetallic properties than arsenic. Correct selection of a dopant can therefore intensify the process by, for example, increasing mutual diffusion during loosening. Preliminary application of a PbS layer onto an oxidizable InP surface has demonstrated good results. Here, as in the case of oxidation of similar heterostructures based on silicon and gallium arsenide, the process begins with the formation of a sulfate skeleton to which indium phosphate and possibly $InPO_4$ and $PbSO_4$ phases attach. Indium sulfides form on the inner interface, which sharply reduces the concentration of indium in the films and frees them of unoxidized indium. Not only is the layer formation process accelerated by a factor of 4 to 6, but the films' electric strength is also increased significantly. Antimony has turned out to be the best cation former for gallium arsenide, and sulfur has been found to be the best anion former. References 90: 65 Russian, 25 Western.

An Investigation of the Products Formed on Molybdenum-Containing Catalysts From Aromatic Hydrocarbons

[Article by L.N. Storozheva, M.A. Lurye, and V.V. Sarayev, Petrochemical and Coal Chemical Synthesis Institute, Irkutsk State University; UDC 5 4 1 . 1 2 8 . 1 3 : 5 4 2 . 4 6 : [5 4 6 . 7 7 ' 7 3 ' 6 2 1 - 44+547.652]:546.261]

[Abstract] The authors of the study reported herein examined the condensation products formed on molybdenum-containing catalysts from aromatic hydrocarbons. Commercial Al-Mo and Al-Co-Mo catalysts containing 12.5 +/- 0.5% (mass) MoO_3 were coked in a continuous reactor at 450, 520, and 600° at an H_2 pressure of 0.5 MPa and with a space velocity of 0.5/h (with respect to the liquid) for half an hour. Binary mixtures of 1- and 2-methyl naphthalene with benzene served as the raw material. After the raw material had been fed into the reactor, the coked catalysts were blasted with inert gas and subjected to vacuum treatment at 100°. The specimens were subjected to EPR spectroscopy, thermal analysis, and IR spectroscopy. The combustion method was used to determine the content of condensation products in the catalysts. The EPR data obtained demonstrated that the condensation products possess paramagnetism and give off a signal at $\Delta H \approx 5$ gauss and g = 2.0039. After the soluble fractions were removed, the concentration of paramagnetic centers in the condensation products increased by a factor of 5 to 6, which was in good agreement with published data regarding the effect of oxygen on the EPR spectra of condensation products formed from aromatic hydrocarbon products on an oxide molybdenum-containing catalyst. This paramagnetism was attributed to the presence of a system of conjugate bonds, and the observed increase in the concentration of paramagnetic centers after the soluble fractions were removed was attributed to the fact that the latter were less condensed than the carboids. The properties of the condensation products formed were determined to be largely dictated by the position of the methyl group in the starting compound. It was hypothesized that in the case of 1-methyl naphthalene, the carboids maintain the "island" nature of their arrangement on the catalyst surface throughout the entire temperature interval studied and that their concentration of paramagnetic centers remains virtually unchanged. The formation of "continuous"-type structures from 2-methyl naphthalene, on the other hand, is explained in terms of the increase in the carboid content and increase in the concentration of paramagnetic centers as the temperature is increased. Figure 1; references 17: 11 Russian, 6 Western.

Total Refining of Gas Catalystic Cracking Gas Oils

927M0069C Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 8, Aug 91 pp 6-7

[Article by M. I. Rustamov, N. M. Indryukov, I. P. Sidorchuk, and A. V. Varina, Petrochemical Processing Institute imeni Yu. G. Mamedaliyeva, Baku; UDC 665.753.4+665.777.2(4+678.049):665.644.2-404]

[Abstract] During catalytic cracking of crude oil, considerable amounts of light and heavy gas oil are obtained which are not fully utilized. The light fraction is mostly blended in with diesel fuel, while the heavy fraction is used either as boiler fuel or as stock for technical grade carbon and coke. In the present work a new extraction scheme was developed for more rational utilization of the gas oil. After the mixed gas oils are extracted with furfurol, the raffinate is distilled and the)while the higher boiling fraction becomes feedstock for further catalytic cracking. The extract is separated into three fractions with the fraction boiling below 300° being alkylated with propylene into other hydrocarbons. The 300-420° fraction is used to make carbon, and the higher boiling (420° C) fraction becomes stock for coke. The scheme was developed for conditions existing at the Novo-Bakinsk Oil Refinery and is recommended as a means for deriving more useful products from catalytically cracked gas oil. References 7 (Russian).

Combined Reforming of Gasoline Fractions

927M0069D Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 8, Aug 91 pp 8-9

[Article by K. G. Abdulminev, A. F. Akhmetov, M. A. Tanatarov, and A. N. Voloshin, Petroleum Institute, Ufa; UDC 665.644.4]

[Abstract] A basic trend in the development of catalytic reforming lies in raising the temperature and lowering the pressure in the reaction zone. However, excessive changes in these parameters leads to rapid catalyst coking, especially in the third reactor operating under severe conditions. To maintain the required level of activity, the catalyst is used in a fluidized bed and continuously regenerated. The non-aromatic component of the catalyzate from heavy reforming, containing 60-70 percent aromatic hydrocarbons, has a low octane number (55-60). When preparing unleaded gasoline AI-93, 18-20 percent of costly and scarce alkylate must be added to lower the aromatics content and raise the octane number. Apparently, by raising the octane number of the non-aromatic component it is possible to change the isomerizate requirement for commercial grade gasoline. Therefore, development of methods to increase the octane number on the non-aromatic reforming component has great practical interest. One such method consists of a two-stage combined reforming process, where 85-180° C b.p. fraction from straight-run West Siberian crude is catalytically reformed under mild conditions (480° C; 2.5 MPa pressure; 3 hourly space

velocity) in two reactors, each charged with alumina-platina and polymetallic catalysts in a stationary bed. Here, the naphthenic, and to some extent aliphatic hydrocarbons are aromatized. After cooling, the reaction products enter a gas separator from which circulating hydrogen-containing gas is directed to the second stage of the process (in a third reactor), while the liquid catalyzate is directed to a fractionating column where the C_5-C_6 and C_7-C_{10} hydrocarbons are separated. The C_7-C_{10} hydrocarbons obtained in the first stage become feedstock for the second stage which takes place under more severe conditions. Combining the second stage catalyzate with the C_5-C_6 hydrocarbons of the first stage results in a blending component for high octane gasoline. Figure 1.

Raising Stability of Blended Diesel Fuels with Composite Additives

927M0069F Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 8, Aug 91 pp 12-14

[Article by I. A. Golubeva, T. S. Gromova, N. M. Malko, Ye. V. Gritsenko, and I. V. Petrov, Petrochemical and Gas Industry Institute imeni I. M. Gubkin, Moscow; Petroleum Refining SRI (A- U), Moscow; UDC665.7.038.5]

[Abstract] Domestic standards fail to provide for addition of stabilizing additives such as antioxidants, dispersants, and metal deactivators to diesel fuels. However, after prolonged storage, insoluble products may form in these fuels and gum formation on injector orifices has been observed in heat-stressed engines. These symptoms are further intensified when using blended fuels containing unstable components such as non- hydrofined gas oil from catalytic cracking. It then becomes imperative to add additives which inhibit oxidation and prevent sedimentation to these fuels. In the present work it was demonstrated that a composite additive of the MING-1 series containing an aminophenolic antioxidant and a dispersant at 0.015 percent concentration and 1:3 anti-oxidant to dispersant ratio effectively improves the chemical stability of diesel fuels containing non-hydrofined light gas oil during storage. At high temperatures the effectiveness of the additives depends on the composition of the dispersant. Figures 4; references 2 (Russian).

Effects of Anti-Corrosion Coatings on Tanks on Jet Fuel Quality

927M0069G Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 8, Aug 91 pp 14-15

[Article by V. A. Mityagin, V. S. Yakovlev, N. N. Zakharovova, and A. P. Kryuchkova, Chemistry SRI (State); UDC620.197.3:620.197.8]

[Abstract] The inner surfaces of steel tanks are subject to corrosion from oil products stored in them. Although oil

products, particularly motor fuels, are not directly corrosive to metals, they combine with oxygen or sulfur to form corrosive by- products as revealed by analysis of sediments. Although state standard GOST 1510-84, dealing with labeling, packing, and transporting of oil and oil products specifies storage of oil products in metal tanks having a protective coating, a great number of tanks now in use lack this protection. In some cases zinc coatings are used, although they present toxic and explosive hazards. Other protective coatings have been developed but before they can be recommended, they must be tested for their effects on the quality of the oil product stored in them. In the present work three epoxy coatings, two vinyl chloride/vinyl acetate copolymers, and zinc-coated liquid glass (Silicazinc-2) were tested. The epoxy and copolymer coatings had no negative effects on the quality of jet fuel and are recommended as protective coating for the above purpose. References 7 (Russian).

Lubricating Properties of Oils Containing Solid Additives at High Temperatures

927M0069H Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 8, Aug 91 pp 15-16

[Article by K. M. Badyshtova, Ye. G. Makhovkin, A. P. Kozlovtsev, S. V. Obraztsov, and I. A. Pogodina, Kuybyshev Branch Petroleum Products SRI (A-U); UDC665.765-404:621.89:543]

[Abstract] Lubricating oils having high levels of thermooxidation and lubricity at high temperatures are needed to facilitate operation of heavily loaded gear boxes of metallurgical equipment operating at high temperatures. In foreign countries such lubricants contain solid additives such as graphite, molybdenum disulfide, or polytetrafluoroethylene, which remain functional at temperatures exceeding 200° C. The domestic assortment includes gear oil series IRp, ISP, ITP, and I100R containing organic oil-soluble functional additives. Oil IRp-150 is used as a gear lubricant operating at moderate to high temperatures. Domestic industry does not produce gear oils containing solid lubricant additives for operation at extreme conditions. In the present work a study of the effects of high temperature on the lubricating properties of three domestic oils with and without graphite or molybdenum disulfide at 50 and 250° C shows that these additives have different lubricating mechanisms on surfaces under friction. Oils ITsp-20 and IMSp-220 are not suitable for lubricating heavily loaded gear boxes. The resulting data may be used to develop new oils containing functional and solid additives. Figure 1; references 7: 3 Russian, 4 Western.

Low Sulfur Crudes and Gas Condensates from Orenburg Oblast

927M00691 Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 8, Aug 91 pp 21-25

[Article by S. G. Khabibullin, L. Z. Garipova, A. A. Voltsov, and F. M. Kasimova, Petroleum Products SRI, Bashkir; UDC665.61.03]

[Abstract] Several new oil deposits have been discovered in the southern part of Orenburg Oblast. The deposits have been characterized as anticlinic, stratified-anticlinic, and stratified under high pressure and with a significant gas factor. The crudes and gas condensates have low densities, insignificant sulfur, metals, and resin-asphaltene content, high yields of light fractions and high melting point paraffins. The physical- chemical characteristics of crudes taken from various strata are presented in tables. The gasoline fraction (28-180° C) has a yield of 25.8-48.5 percent based on the crude, although the octane number is low (40-47, motor method) owing to the significant content of paraffinic hydrocarbons (58-65 percent of the fraction). The fractions serving as catalytic reforming feedstock are low in naphthenic hydrocarbons. Catalytic reforming under normal conditions yields only A-76 gasoline; to obtain high octane components, more rigorous conditions or a moving bed catalyst with frequent regeneration are required. The kerosene fractions do not conform to the norms for aviation fuel, although they could be used for production thereof. The crudes have a significant diesel fuel fraction (30-45 percent) with high cetane numbers and low sulfur content making them suitable for summer and winter grade diesel fuels without hydrofining.

Effect of Catalytic Cracking Conditions on Characteristics of Light Gas Oil

927M0069J Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 8, Aug 91 pp 25-28

[Article by V. A. Stankevich, T. Kh. Melik-Akhnazarov, T. N. Mitusova, I. Ya. Perezhigina, A. M. Senekina, L. Ya. Vlasenko, T. M. Stepanova, and V. S. Yedigarova, Petroluem Products SRI; Moscow Petroleum Refinery; UDC665.644.2]

[Abstract] Light gas oil from catalytic cracking (LGKK), the 195-270° C fraction, is target production at Unit G-43-107 of the Moscow Petroleum Refinery and is earmarked as a component for diesel and boiler fuel. However, research shows that use of LGKK as a component of diesel fuel requires raising its chemical resistance by either hydrofining or addition of antioxidants. Selection of the upper limit of fractionation depends on the quality requirements of heavy gas oil from catalytic cracking (TGKK), a source for production of technical grade carbon. Depending on the process conditions, LGKK yield ranges from 11 to 17 percent based on the feedstock. Aside from process conditions, the properties of the catalyst and feedstock also affect the characteristics of LGKK, as well as the degree of hydrofining. Cetane number, density, fraction composition, iodine number and other properties are given for various runs on a pilot plant installation. Figures 3; references 7 (Russian).

Study of Structure Formation in Oils by EPR-Spectroscopy

[Article by V. A. Kuznetsov, N. N. Popova, T. Yu. Mikheyeva, I. O. Kolesnik, A. A. Gureyev, and E. D. Mamdeova, Petrochemical and Gas Industry Institute imeni I. M. Gubkin, Moscow; Petroleum Products SRI (A-U); UDC665.765-404.033]

[Abstract] Antioxidants such as ionol are known to have little effect on non-refined oils. This is explained as a tendency of ionol to form associates with resinous and aromatic compounds, especially polycyclics. However, the true reasons for the passive action of aromatic compounds and non-hydrocarbon oil components on antioxidants have not been sufficiently investigated. In the present work a study was made of the feasibility of using EPR-spectroscopy (spin sonde method) to obtain information on the processes of structure formation in oils not containing additives and in oils inhibited with ionol. Stable nitroxyl radical from stearic acid was used as the spin sonde. Studies made on a transformer oil and an oil from the Novo-Yaroslav Petroleum Refinery demonstrated that EPR- spectroscopy makes it possible to collect data on structure formation processes in oils for a more comprehensive approach to the selection of additive type and its concentration. Figures 3; references 7 (Russian).

Gas and Oil From Coal

[Article by Academician M. V. Golitsyn, Moscow State University]

[Abstract] The origins of oil and natural gas are still under dispute. A majority recognizes the organic theory, while others maintain that hydrocarbons come from the earth's mantle. Still others think that they are derived from coal, and this latter concept is discussed in the present work. For a long time it was considered that coal does not exist in places where oil and gas are present because it was believed that the organic matter from which oil was derived formed from lower forms of plants and microorganisms under aquatic conditions, while coal was formed from higher plants on dry land. This theory started to fall apart in recent postwar years when the first gas condensate deposit was discovered in the Donbass (continental) region. Today, this region contains 46 oil and gas deposits. During the 1960's soviet geologists concluded coal played a significant role in generating hydrocarbons in the West Siberian fields. During its metamorphosis, coal emits an enormous quantity of methane (200-250 cubic meters per ton of coal). This gas then migrates along the coal seam and is either vented to the open air, or trapped in some anticline to form a gas deposit. Mine gas explosions have scattered thousands of cubic meters of coal and rock. Coal is also capable of generating liquid hydrocarbons if it contains lipoid microcomponents (spore casings, pollen, cuticles, or resinous bodies of higher plants) and sapropelic material formed from lower plants under aquatic conditions. Figures 2.

Copolymer Depressor Additives for Regenerated Lube Oils

[Article by R. A. Terteryan, V. I. Aksenov, O. M. Ponadiy, A. I. Bukhter, and L. K. Davidyan, Petroleum Refining SRI (A-U), Moscow; UDC 66.022.37: 678.763.43(047)]

[Abstract] The search for an effective pour point depressant occupies an important position in resolving the production of regenerated lube oils. Regenerated oils I-20 and I-40 have higher pour points than machine oils I-20A and I-40A, in accordance with GOST 20799-75 standard. A depressant additive for these oils must provide a pour point depression of -15° C without affecting viscosity or flash point. Such an effect may be achieved by using domestic depressant additives PMA "D", AzNII-TsIATIM-1, or AFK. However, the latter two have metals present in the molecules causing ash to form which has a negative effect on the quality of the oil. In the present work ash-free depressants were prepared from ethylene-vinyl acetate and ethylene-maleic acid anhydride copolymers. Tests show that the new depressants, synthesized from available materials, are as effective as the above ash-forming additives. Figure 1.

Styrene-Containing Polymers as Accelerators for Preparing Binder from Bottoms Stock

[Article by Ye. V. Rogozina, I. M. Kanevskiy, A. N. Aminov, and M. Ya. Grinberg, Yaroslavl Polytechnical University; UDC 665.637.8.002.33]

[Abstract] One of the factors limiting road construction is the limited availability of bitumen suppliers. Therefore, much of the binder is produced directly by road building organizations by oxidation of bottoms stock in local units. It has been observed that the rate of the process and the quality of product may be increased by introducing polymers containing styrene or copolymers of styrene and other olefins. In the present work the effects of adding the above on the kinetics of bottoms stock oxidation were studied in a laboratory scale compression type batch reactor at 220-230° C and 1-1.5 liters per min.kg air throughput rate. The results demonstrate that addition of styrene to the bottoms stock lessens the time required for preparation of the binder and improves its quality. Figures 2; references 2 (Russian).

Investigation of the Process of Solidification of a Polymer Coating on a Lightguide by the EPR Method

[Article by G.G. Devyatykh (academician), Yu.D. Semchikov, Z.A. Tikhonova, S.Yu. Kashayev, N.A. Kopylova, and A.Yu. Laptev, Institute of the Chemistry of Ultrapure Substances, USSR Academy of Sciences, Nizhniy Novgorod, and Chemistry Scientific Research Institute, Nizhegorodskiy State University imeni N.I. Lobachevskiy; UDC 541.64:539.2]

[Abstract] The authors of the study reported herein examined the process of the solidification of a polymer coating on a lightguide by the EPR method. The photohardening composite used consisted of DO4-TA oligoetherurethane acrylate (70%), ethylene glycol diacrylate (20%), 2-ethylhexyl acrylate (10%), and the solidification photoinitiator 2,2-dimethoxy-2-phenylacetophenone. The thermographic method was used to study the photopolymerization kinetics. The solidification process was conducted either in ampules or under conditions simulating the application of a polymer coating to fiber. In both cases the EPR method (with a Bruker etalon) was used to measure the concentration of radicals in the solidifying composite, and the degree of solidification was determined by the gravimetric method. The EPR signal increased as soon as irradiation of the reaction mixture began and persisted for a long time after the irradiation had been completed. The concentration of radicals and degree of monomer transformation remained similar in slope. The photosolidification process was distinguished by the fact that it was not subordinate to the square-root rule that is valid for chain radical reactions. In the case of a photoinitiator concentration above 1% the rate of polymerization and radical concentration not only did not increase proportionally to $C_{photoinit}^{0.5}$, but actually decreased. A reaction rate concentration of about 4.5×10^2 mol/l/s was discovered (cf. the previously published reaction constant of 6×10^2 mol/l/s for linear polymerization of acrylates). The solidification of a polymer coating on a lightguide was determined to occur primarily outside the illumination zone as a result of the reaction of a growth of long-lived radicals. The solidification process was found to be a dark process in which the polymerization reaction proceeds on the radicals immobilized in the lattice in accordance with a "living chain" mechanism. Figures 4; references 5 (Russian).

Distinctive Features of the Structural Transitions in Poly-N-Alkylmethacrylamide Macromolecules in Water When Heated

[Article by Ye.V. Anufriyeva, M.G. Krakovyak, R.A. Gromova, V.B. Lushchik, T.D. Ananyeva, and T.V. Sheveleva, High-Molecular Compounds Institute, USSR Academy of Sciences, Leningrad; UDC 541.64:539.199]

[Abstract] The authors of the study reported herein examined the structural transitions occurring in macromolecules of poly-N-alkylmethacrylamide [PAMA] in water during heating. Their primary object in so doing was to determine the extent to which structure formation in macromolecules of water-soluble polymers is sensitive

to the structure of the alkyl groupings. The polarization luminescence method was used to measure the relaxation time characterizing the intramolecular mobility of the macromolecules. Luminescing organic ions of acridine orange and auramine were used as indicators sensitive to a change in local concentration of nonpolar groups in macromolecules of water-soluble polymers. The fraction of bound indicator was determined by the polarization luminescence method. The studies were conducted in diluted solutions containing 0.02% PAMA to reduce the contribution of the intermolecular contacts. The studies revealed that in macrimolecules of PAMA-1, the presence of a methyl group at the nitrogen atom does not result in any changes in the polymer's intramolecular mobility that would indicate a change in intromacromolecular structure even when the aqueous solutions were heated all the way to 100°C. Structural transitions were detected in macromolecules of PAMA-2 and PAMA-3 when heated. The temperature interval of the transition shifted to the low-temperature side as the length of the alkyl substituent increased (80 and 32°C, respectively). In macromolecules of PAMA-4 the intramolecular mobility was significantly inhibited, even at 25°C ($\tau_{intramolec. mob.}$ = 11 ns for PAMA-1 and PAMA-2, 16 ns for PAMA-3, and 110 ns for PAMA-4). Additional studies were then conducted to determine the type of intramolecular structure formed in PAMA macromolecules in water when heated. Analysis of the data obtained revealed that the interval of the structural transition does not depend on the molecular mass of the polymer. This was taken as an indication that closely spaced alkyl groups that intensify upon heating are the initiator of the structural organization of the molecules studied. The increase in τ characterizing an increase in intramolecular inhibition is accompanied by a plateau. A comparative study of PAMA-3-line and PAMA-3-iso showed that both undergo a cooperative structural transition in water when heated. Unlike the structured elements of PAMA-e-line, however, the globular structure formed when PAMA-3-iso molecules are heated is not maintained when the heated solution is cooled. The studies thus revealed that the number of carbon atoms in the N-alkyl substituents of the PAMA links is not the only factor affecting the distinctive features of the structural transformations of macromolecules in water during heating; their location relative to one another is important as well. Figures 4; references 8: 6 Russian, 2 Western.

The Effect of Sulfating on the Electron Acceptor Properties of a ZrO₂ Surface

[Article by Ye.V. Lunina, Ye.Yu. Badina, N.N. Kuznetsova, and G.L. Markaryan, Moscow State University imeni M.V. Lomonosov; UDC 541.183:543.422: 546.831-31'226]

[Abstract] The authors of the study reported herein used the EPR method to examine the electron acceptor properties of ZrO_2 and ZrO_2-SO_4^{2-}. The study specimens were prepared by precipitation by ammonia from an aqueous solution of zirconium oxychloride followed by careful rinsing, drying in air for days, and roasting at a temperature of 770 K for 5 hours. The specimens were modified with sulfate ions by treatment with a 0.5 M solution of H_2SO_4. The precipitate was filtered off, dried in air, and roasted at a temperature of 870 K for 3 hours. The Brunauer, Emmett, and Teller [BET] method was used to determine the specific surface of the specimens. Values of 130 and 91 m²/g were found for ZrO_2 and ZrO_2-SO_4^{2-}, respectively. The EPR method was used to study the electron acceptor properties of the specimens' surfaces. 2,2,6,6-tetramethylpiperidine-1-oxyl was used as a probe molecule. The specimens were roasted at a specified temperature between 725 and 925 K in air for 2 hours and then in a vacuum of 10^{-3} Pa for 2 hours. The specific surface of the ZrO_2 and ZrO_2-SO_4^{2-} specimens accessible to the 2,2,6,6-tetramethylpiperidine-1-oxyl molecules (as determined by the "paramagnetic grid" method) amounted to 10 m²/g. The quantity of electron acceptor centers causing a shift in electron density (type 1 centers) was then estimated. In the case of ZrO_2 values of 1.6 x 10^{17} and 2.1 x 10^{17} center/m² were obtained respectively for specimens roasted at 725 and 925 K, respectively. Sulfating the surface of ZrO_2 was found to result in a slight increase in the concentration of type 1 adsorption centers; a value of 2.3 x 10^{17} centers/m² was obtained for the ZrO_2-SO_4^{2-} specimens tested. The sequential absorption of 2,2,6,6-tetramethylpiperidine-1-oxyl and pyridine on ZrO_2 and ZrO_2-SO_4^{2-} surfaces was also studied. The concentration of centers capable of forming complexes with total charge transfer (type 2 centers) on the surface of ZrO_2-SO_4^{2-} was significantly higher than the amount of type 1 acceptor centers present. As the roasting temperature was increased from 725 to 925 K, the number of type 2 centers more than doubled. The concentration of type 2 acceptor centers on the surface of ZrO_2-SO_4^{2-} reached 9 x 10^{17} centers/m², which is close to the total acidity of a ZrO_2-SO_4^{2-} surface as determined elsewhere. Thus studies thus indicated that acceptor centers capable of forming centers of total charge transfer appear on a zirconium oxide surface only after it has been modified by sulfate ions and that these centers likely exert a significant effect on the catalytic properties of ZrO_2-SO_4^{2-}. The study results were interpreted as favoring the hypothesis of the superacidic nature of active centers on a sulfate ion-modified ZrO_2 surface. Figure 1, tables 2; references 15: 11 Russian, 4 Western.

Chlorination of a Ternary Copolymer of Ethylene, Propylene, and Dicyclopentadiene

[Article by Ye.T. Pankratova, G.G. Yegorova, Anke Shvendel, V.A. Kazantseva, T.S. Kabina, and S.B. Salnikov; UDC 541.64:547.313.2]

[Abstract] In view of the commercial importance of chemical modification of polymers by the method of chlorination, the authors of the study reported herein examined the chlorination of a ternary copolymer of ethylene, propylene, and dicyclopentadiene with and without an diacetyl oligoazine additive. The study ternary copolymer was chlorinated with molecular chlorine in the presence of a chloroform-insoluble fraction of oligoazine with $M_n \simeq 1,350$. According to PMR spectroscopy data, the study copolymer contained 62% (molecular) ethylene and 36.5% (molecular) propylene links, as well as 1.5% (molecular) dicyclopentadiene links. The chlorination was performed in darkness at 20°C in a carbon tetrachloride solution as described elsewhere. The reaction products were determined by reprecipitation by adding the filtered reaction mixture to a standard. The reaction products were also subjected to IR spectroscopy analysis in chloroform; the gel and sol fractions were isolated as described elsewhere. Increasing the oligoazine to 4-6% (by mass) was found to result in an increase in chlorination efficiency. Non-oligoazine-initiated chlorination of the study copolymer did occur, but the rate and depth of the reaction were both much lower than reactions initiated by oligoazine. As has been reported elsewhere, the role of oligoazine in the chlorination of a saturated polymer was found to lie in the generation of chlorine radicals formed as a result of the decomposition of the donor-acceptor complex of oligoazine with chlorine. The chlorine radicals appearing in the system led to the development of a process of substitutive chlorination based on a free-radical mechanism. The studies led the researchers to the hypothesis that when the study copolymer is chlorinated in the presence of oligoazine, parallel complexing and substitution reactions also take place and that the former of the two predominates in the early stages. Gel formation was deemed the distinctive feature of the process of chlorination of the study copolymer in the absence of oligoazine. The nature of the structuralization process occurring in the early stages of chlorination was found to be the same regardless of whether oligoazine was present. The role of oligoazine as an inhibitor of gel formation was explained as follows: The oligoazine present in the reaction system may enter into a complexing reaction with the macroradical at the dicyclopentadiene chain, acting somewhat like an "interlayering" that stabilizes the macroradical and thereby impedes the rapid recombination of the two macroradicals in the copolymer. Under such conditions, recombination of the macroradical with the chlorine radical would be a more contributory factor. If this were the case, increasing the amount of oligoazine in the system during chlorination of the study copolymer should result in suppression of the structure formation reaction. In fact, the researchers demonstrated that increasing the oligoazine in the reaction zone by a factor of 1.5 resulted in a reduction in the characteristic viscosity of the chlorinated study copolymer by a factor of 2. This was explained by the fact that the ratio of the destruction and grafting rates changed as a function of the destruction rate. Thus, the only difference between the processes of chlorination of copolymer

of ethylene, propylene, and dicyclopentadiene with and without an diacetyl oligoazine additive lay in the rates of the structure formation reaction, and those depended largely on the content of oligoazine in the system. Figures 5; references 11 (Russian).

Dynamics of the Molecular Mass Distribution of Linear Polymers

[Article by V.P. Danilchuk, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Chernogologka, Moscow Oblast; UDC 541.64:53]

[Abstract] Most of the large number of recent publications devoted to the kinetics of the molecular mass distribution of polymers have dealt with the case where the original reaction mixture contains only monomers. The form of molecular mass distribution of the resultant macromolecules and its time dependence have, for example, been determined for the case of a starting reaction mixture consisting solely of reaction monomers. This article presents the corresponding exact analytical solutions for irreversible processes of the polycondensation and destruction of linear polymer molecules. The generating function method is used to find the dependence of the molecular mass distribution on the degree of transformation or time. A total of 30 equations are presented. The author concludes by noting that the solutions found remain unchanged regardless of the time dependence of the parameters α and β provided that all the end functional groups have an identical probability of reacting with one another at any given moment and that, consequently, the probabilities of the breaking of all of the interlink bonds in a linear polymer are identical (the Flory principle). Specifically, the analysis presented will be altered somewhat in the case where there is a significant excess of low-molecular weight product in the system being analyzed. References 2: 1 Russian, 1 Western.

The Entropy of Statistically Uniform Lattices of Infinitely Long Polymer Molecules

[Article by V.V. Malev, Cytology Institute, USSR Academy of Sciences, Leningrad; UDC 541.60+539.2]

[Abstract] The author of this article has worked to describe rather thick bundles of polymer molecules (ideally of infinite length) that are each potentially capable of bending (without the formation of loops) when their circle contains vacancies not occupied by other bending molecules. The cross section of the bundle is represented in the form of a correct lattice of sites with the coordination number c and with the lattice constant λ_0. At a

distance $d_0 \geq \lambda_0$ from the starting cross section, all of the bundle's molecules are oriented along the normal to this cross section, and at the point d_0 there may or may not be a jumplike bending of a molecule accompanied by a jump to a neighboring vacant space while the perpendicular orientation of the molecule axis is maintained at the now-doubled distance $2d_0$, where the next bend may occur, etc. In the case of bundles that are infinitely diluted from the standpoint of polymer molecules (where the probability of encountering the latter may be ignored), the trajectory of the sequential displacements of a molecule axis from its initial position will obviously be given by a pattern of random movement or Brownian motion. To illustrate his proposed method, the author confines himself to the case of a one-dimensional lattice. In other words, he determines the cross section of the study bundle as a system of sites that are equidistant from one another, each having two neighboring sites, and all located on some surface that is not necessarily a plane. Assuming that the number of molecules in the bundle equals $n < N$, the author proceeds to calculate the statistical probability W of such a system under the condition that its length D_0 is rather large. This in turn allows him to limit himself to estimating the number of methods used by the system to jump from some l-th segment to the next, i.e., $(l+1)$-th segment. The author concludes by stating that the analysis presented may be further developed so as to become exhaustive and that the procedure presented may further be generalized to the case of an arbitrary coordination number c (although this will admittedly result in problems related to the need to give consideration to the increasing number of pq-configurations. Reference 1 (Russian).

Diffusion of Low-Molecular Substances in Two-Phase Block Copolymers Containing Rigid and Flexible Blocks

[Article by M.A. Krykin, A.N. Ozerin, I.P. Storozhuk, M.N. Tulskiy, V.I. Muromtsev, and N.F. Bakeyev, corresponding member USSR Academy of Sciences, Physicochemical Scientific Research Institute imeni L.Ya. Karpov, Moscow, Moscow Chemical Technology Institute imeni D.I. Mendeleyev, and Atomic Energy Institute imeni I.V. Kurchatov, Moscow; UDC 533.15]

[Abstract] The development of membrane technology has caused increased interest in processes of the diffusion of low-molecular substances and block copolymers. Microheterogeneous materials with virtually total microphase separation have become extremely popular thanks to their selective permeability (owing to their continuous flexible microphase) and significant mechanical strength (owing to domains of a dispersed rigid phase). In view of these facts, the authors of the study reported herein worked to establish a link between the local diffusion properties of the flexible microphase of block copolymers and the degree of "nonequilibrium" of

its packing. As research objects they used polyblock statistical polysulfone-polybutadiene block copolymers containing rigid blocks of aromatic oligosulfone and flexible blocks of oligobutadiene. 4,4'-Diphenylmethane-diisicyonate served as a chain extender. The block copolymers were synthesized in accordance with a method presented elsewhere. The content of flexible polybutadiene blocks was varied from 20 to 90% (by mass), while the molecular mass of the block copolymer overall was kept at approximately 5.5×10^4. Specimens in the form of granules with a diameter of about 1 mm were prepared from block copolymer solutions in chloroform. The laws governing diffusion of low-molecular substances were studied by way of the example of n-hexane by the method of nuclear magnetic resonance with a pulsed magnetic field gradient. The block copolymers were saturated with hexane for 2 to 3 days in a covered box and then sealed in a 6-mm-diameter glass ampule that in which the pressure of saturated C_6H_{14} vapors was constantly maintained. The studies performed established that the presence of a small number of vigorously interacting molecular fragments between the blocks of the block copolymer's rigid and flexible phases resulted in nonequilibrium flexible block conformations, the appearance of an additional free space, and the "acceleration" of the processes of diffusion of the low-molecular substance in the block copolymer's flexible microphase. Figures 2; references 6: 6 Russian, 1 Western.

An Electrochemical and Spectral Study of Solid AgI and LiI Electrolytes Doped With Polymers and Copolymers of 2-Vinylpyridine With N- and S-Containing Monomers

[Article by N.N. Rzhevskaya, A.Ye. Sokolov, A.N. Petrov, V.N. Kreytsberg, and V.L. Tsaylingold, Yarsintex Scientific Production Association; UDC 541.64:543.422]

[Abstract] The authors of the study reported herein used electrochemical and spectral methods to examine solid AgI and LiI electrolytes doped with poly-2-vinylpyridine and copolymers of 2-vinylpyridine and 2-pyridylethyl methacrylate, paratolyl thioethylene, and diethylamino-nethyl methacrylate. The said polymers and copolymers were synthesized as described elsewhere. The silver iodide was produced by mixing iodine dried over Pi_2O_5 with colloidal silver in a stoichiometric ratio and them pouring both components into an argon-blown ampule. The sealed ampule was heated to 423 K for 2 hours. After completion of the synthesis process, the AgI was then doped with the aforesaid polymers and copolymers. Model LiI galvanic cells were also assembled in a box with an isolated argon atmosphere. The conductivity of the pressed solid doped AgI electrolytes was measured, and the specific electric discharge of cathode material based on the specified polymers and polymers and the

coefficient of iodine utilization in the galvanic cell were determined. The electron spectra of the diffuse reflection of the model AgI-(co)polymer systems were recorded on a Specord M040 UVIS recording spectrophotometer. The various spectra were compared in an attempt to explain the nature of the kinetic discharge curves of model LiI galvanic cells with a cathode compound based on the study polymers and copolymers. The reactions occurring as each of the study (co)polymers was used were analyzed individually. The analysis revealed that when a copolymer is added to the electrolyte, the latter's conductivity is improved. Increasing the content of free I_2 formed upon dissociation of polyiodide ions and chains was found to result in a decrease in electrolyte conductivity. Increasing the molecular mass of poly-2-vinylpyridine was found to result in the enlargement of the polymer counter ion, thus accounting for the high stability of polyiodide chains and, accordingly, the high electric conduction of doped electrolytes. Figures 4; references 6: 3 Russian, 3 Western.

Determining the Volume and Density of Inter- and Intrafibrillar Amorphous Components in Partially Crystalline Polymers

[Article by R.L. Khalfin, All-Union Scientific Research Institute of Textile Materials; UDC 541.64:539.26]

[Abstract] The author of this article has worked to refine the method used to determine the volume and density of inter- and intrafibrillar amorphous components in partially crystalline polymers. After analyzing other researchers' approaches to the problem, he proposes a method of determining the density of inter- and intrafibrillar amorphous components of a polymer based on low-angle x-ray diffraction data (in absolute units). A dependence is presented that does not call for any additonal assumptions regarding mass exchange in the amorphous component. Use of the said expression is shown to lead to the conclusion that the density of the intrafibrillar amorphous component is preserved throughout a polymer regardless of its degree of elastic stretching. By way of the example of polyethylene, the author demonstrates that the results of determining the density of intrafibrillar amorphous intervals in elastically stretched specimens by methods of measurement in absolute and relative units coincide. The author cautions that in addition to the error associated with the process of measuring total crystallinity, the method involves an element of indeterminacy K_0 that depends on the characteristic features of the given polymer's structure. Thus, the size and defectiveness of the crystallites and the structure of the amorphous component surrounding them may affect the melting heat, which is used as a basis for determining K_0. The author further comments that for series of specimens of very similar structure, in which case it is possible to determine the melting heat of a

totally crystalline polymer by approximation, the indeterminacy of K_0 will be insignificant. He concludes by noting that his proposed method can only be used in the case of specimens that do not contain micropores. Figures 2, tables 4; references 12 (Russian).

The Effect of Phosphorus-Containing Antipyrenes on the Processes of Coke Formation During the Combustion of Polymer Composites

[Article by C.Ye. Artemenko, L.G. Panova, V.I. Besshaposhnikova, and L.D. Skrebneva, Engels Affiliate, Saratov Polytechnic Institute; UDC 541.64:542.943]

[Abstract] The authors of the study reported herein have examined the effect of phosphorus-containing antipyrenes on processes of coke formation during the combustion of polymer composites. Specifically, they studied the surface structure of coke and distribution of elements in polymer composites and coke obtained by burning (for 30 seconds) specimens of epoxy polymer composites containing different amounts of oxygen (30, 50, and 100 %(vol)) in a gaseous mixture. The study specimens were produced by the method of compression pressing at a temperature of 423 +/- 5 K under a pressure of 8 MPa with a molding-process duration of 300 seconds per millimeter of specimen thickness. Scanning electron microscopy and microprobe analysis on a Superprob-733 equipped with wave spectrometers were used for the studies. The distribution of phosphorus, carbon, and oxygen in the polymer composites and coke was determined by local analysis. The coke formed when polymer composites not containing antipyrenes in their composition were burned was found to have a fine-pore homogeneous structure that did not separate without breaking and whose fiber and polymer matrix were not differentiated. The coke formed when polymer composites containing antipyrene as a part of their composition were burned, on the other hand, was found to have various structures depending on the method used to add the antipyrene to the polymer composite. The coke formed when the antipyrene was added to the polymer composite with a reinforcing fiber was highly porous; it had a "cap" of frothy coke on its surface, while the textile structure of the fiber was retained in its bulk. The frothy coke was easily separated owing to the presence of a gaseous interlayering between the main part of the coke and the frothy coke. There was a general decrease in the amount of volatile products released during pyrolysis of the polymer composite reinforced with antipyrene-modified fiber; however the release of such products was more intense in the interval of the principal stage of destruction than was the case with polymer composites based on the starting (unmodified) fiber. This applies especially to water and carbon dioxide. Analysis of the distribution of elements in the coke showed phosphorus to be present both in the surface layer of the coke and in its bulk. When materials to which antipyrene had been

added with an epoxy resin reinforced by unmodified fiber was burned, the macroporosity of the coke formed was found to be reduced. The textile structure of the fiber under the top layer was found to have experienced a much greater degree of damage, and the material was characterized by a higher combustibility than that of polymer composites to which the same amount of antipyrene had been added but with a reinforcing fiber. The presence of phosphorus in the composition in both cases was thus found to result in structural changes in the coke as compared with the coke of polymer composites reinforced by the starting fiber. The studies thus confirmed that the combustion process does indeed affect coke formation, which is in turn affected not only by the presence of antipyrene but by the method used to add it to the polymer composite and on its subsequent distribution in the polymer composite. When antipyrene was added with binder, the phosphorus diffused from the polymer matrix and into the fiber; however, the data indicated that only the fiber's surface was protected by this diffusion and that it still burned. Another factor reducing the effectiveness of antipyrene and depending on the method used to add it to polymer composites was the amount of antipyrene on the fiber. Polymer composites into which the antipyrene had been added as part of a binder were found to contain less antipyrene than were polymer composites to which an identical starting amount of antipyrene had been added but to which it had been added in the form of reinforced modified fibers. Figures 4; references 3 (Russian).

Interpolymer Complexes of Poly-N-Vinylamides With Polycarboxylic Acids in Solvents With Different Natures

[Article by Ye.V. Anufriyeva, M.R. Ramazanova, M.G. Krakovyak, V.B. Lushchik, T.N. Nekrasova, and T.V. Sheveleva, High Molecular Compounds Institute, USSR Academy of Sciences; UDC 541(49+64)]

[Abstract] The authors of the study reported herein used the method of polarization luminescence to study the intramolecular mobility of interacting polymer chains. Their primary objective in so doing was to establish the laws governing the structural changes in poly-n-vinylamide-polycarboxylic acid interpolymer complexes when various organic solvents for poly-n-vinylamides with different chemical structures are used in place of water. A variety of diluted solutions with polymer concentrations of 0.05 to 0.5% were tested during the studies. The following were used as solvents: water, DMPA, N-methylpyrrolidone, methanol, and mixed water-and-organic solvents. The researchers examined poly-n-vinylamides with side group substituents at the nitrogen atom of varying chemical composition (i.e., poly-N-vinylcaprolactam, poly-N-vinylpyrrolidone, and poly-N-methyl-N-vinylacetamide) and polycarboxylic acids (i.e.,

polyacrylic and polymethacrylic acid). The polymers studied had a molecular mass of 40 to 100 x 10^3. Tests performed on the test specimens confirmed that when organic solvents are used in place of water, the structure of the interpolymer complexes is completely destroyed. The two-strand structure of the specimens was retained in the nonamide solvent methanol. In the amide solvent N-methylpyrrolidone the two-strand structure was completely destroyed; it was partially destroyed in DMPA. The studies also established that molecular-type interpolymer complexes form when all of the study poly-n-vinylamides are reacted with polymethacrylic and polyacrylic acids in water and methanol. A supermolecular-type interpolymer complex was observed to form in the systems poly-N-vinylcaprolactam-polyacrylic acid and poly-N-vinylcaprolactam-polymethacrylic acid in the solvent DMPA. The studies thus demonstrated that only intermolecular contacts capable of competing with polymer-solvent contacts result in the formation of molecular-type interpolymer complexes. The formation of molecular-type interpolymer complexes (i.e., the formation of interpolymer bonds) in diluted solvents in the system polymethacrylic acid-poly-n-vinylamide is evidently impeded by the screening effect of the massive substituent at the C=O group of poly-N-vinylcaprolactam. In the system polyacrylic acid-poly-N-vinylcaprolactam, the partial ionization of polyacrylic acid is a second factor impeding the formation of contacts. Figures 4, table 1; references 11: 9 Russian, 2 Western.

Orientation Processes Occurring When Polymers Are Poured and Their Effect on Mechanical Properties

[Article by M.V. Buy, Ye.N. Sokolov, A.V. Rogachev, and A.K. Novikov, Institute of the Mechanics of Metal and Polymer Systems, Belarus Academy of Sciences, and Gomel Affiliate, Elorma Scientific Production Association; UDC 541.65:539.3]

[Abstract] The authors of the study reported herein worked to develop a model describing the orientation effects occurring when a polymer is crystallized as it flows along the shaping surface. The study specimens were produced from type 210-01 high-density polyethylene by using a DG-3231 automatic thermoplastic machine. Accessories were used that made it possible to use the method of injection molding and a technique involving having the melt flow along the molding surface. The mechanical properties (tensile strength, relative elongation) of the study specimens were determined by stretching the specimens in accordance with All-Union State Standard GOST 11969-80 on a ZD 10/90 stretching machine at a rate of 0.9 mm/s. The degree of the macromolecules' orientation was estimated by the method of polarization IR spectroscopy (on a UR-20) based on the dichroism of the band at 1,892 cm^{-1} and by

microcalorimetry (on a DSM-2 microcalorimeter) based on the integral melting heats of the low- and high-temperature (oriented) phases. Microsections of the polymer were taken to determine the distribution of the orientation of the macromolecules throughout the thickness of the specimen. The crystallization conditions were varied by using molding surfaces of different thicknesses and by varying the temperature and time parameters of the process. The experimentally obtained results were used along with a previously published molecular-kinetic analysis of the characteristics features of conditions of a flow along the polymer interface. The said analysis, which indicated that the main competing processes affecting the structure of the oriented layer of the melt are the mechanical stresses in the said layer and the thermal relaxation in the liquid phase, was used by the authors of the present study as the point of departure for their derivation of a series of expressions explaining the dimensional effects of the mechanical properties of poured polymer materials. The theoretical and experimental studies performed established that the parameters of orientation crystallization by and large determine the mechanical properties of polymer products, as well as their dependence on process parameters and molding conditions. The studies performed confirmed that the technique of flowing the polymer melt along the surface of the mold results in products with a higher tensile strength than are produced by the method of injection molding. The dependence of tensile strength on specimen thickness is an extremal dependence: the ultimate strength of the poured polymer products studied was found to be at its maximum at a thickness of $2\Delta \approx 2$ mm. This dimensional effect was shown to be linked to a change in the integral degree of the specimens' orientation as their thickness increases. The tensile strength of test products produced by the technique of flowing the melt along the mold's surface was found to decrease as the temperature of the polymer added to the mold was increased. Figures 3, table 1; references 8: 7 Russian, 1 Western.

Computer Simulation of the Local Dynamics of a Polymer Chain in a Liquid Crystal-Type Orienting Field

[Article by A.A. Darinskiy, Yu.Ya. Gotlib, A.V. Lyulin, and I.M. Neyelov, High Molecular Compounds Institute, USSR Academy of Sciences; UDC 541.64: 139(199+2)]

[Abstract] The authors of the study reported herein developed a computer simulation of the local dynamics of a polymer chain in a liquid crystal-type orienting field. Specifically, they modeled the motion of a freely articulated chain consisting of N rigid links (N = 16) connecting N + 1 centers of viscous drag with a friction coefficient of ξ. The simulation was based on the method

of Brownian dynamics, according to which the surroundings of the polymer chain (solvent or links of neighboring chains) are described by averaging as a viscous medium and source of random Brownian forces. The motion of the polymer chain in the external field is subject to a Langevin equation. The case of high viscosity, in which the inertial element may be ignored, is considered. The equation developed to describe the motion of the aforesaid polymer chain solvent was solved numerically on a Cyber-172 computer by using an algorithm that has been detailed elsewhere. During the course of their simulation, the researchers investigated the anisotropy of the equilibrium properties, local forward and rotational motion of the change, and the dependence of the said anisotropy on the magnitude of the external field and on the position of the given link in the chain. The equilibrium characteristics of a freely articulated chain are modeled by using a previously published order parameter for the links of a chain and a dumbbell. The simulation revealed that the mobility of the chain's links in an external field is greater than that predicted by the Kramers theory. An analytical expression was also derived for calculating the average time of passage of a dumbbell-link through an external potential barrier. Figures 5, tables 2; references 11: 9 Russian, 2 Western.

An Additive Scheme for Determining the Activation Energy of Low-Temperature Transitions in Polymers

[Article by Yu.I. Matveyev and A.A. Askadskiy, Elementoorganic Compounds Institute imeni A.N. Nesmeyanov, USSR Academy of Sciences; UDC 541.64:539.199]

[Abstract] Predicting the durability of polymers, their acoustic and relaxation properties, and their sorption and permeability requires knowing the activation energies linked to the different transitions in polymer systems. If a polymer is being looked upon as a linear system, a set of activation energies generally linked to the motion of a specified group of atoms is generally considered. If the same polymer is viewed as a nonlinear system, it is only necessary to know the activation energy of just the elementary acts related, for example, to the migration of the atoms in a repeated isomer from one state of equilibrium to another and that is generally linked to the activation energy of the γ-transition. All other relaxation times caused by other transitions are expressed through the activation energy being sought and through the temperature coefficients determined by the parameters of the nonlinear model. Before these previously existing models can be used to calculate specific polymer systems, the way in which the model's parameters are linked to the chemical structure of the repeated link must be known. Among the specific parameters that must be known are the viscosities included in the Aleksandrov-Lazurkin nonlinear model. In view of

these facts, the authors of the study reported herein worked to show that the set of relationships published in one of their own previous communications may be used to derive expressions to determine the activation energy that figures in the temperature dependences of the relaxation times (viscosity). They base their analysis on a nonlinear model of a polymer body and use results obtained by using the theory of molecular similarity to derive an additive expression for determining the activation energy of a γ-transition. Through their analysis, the authors demonstrate that the said activation energy is linked by simple dependences with the vitrification temperature and that an additive scheme may thus be used to describe it. The results obtained by using the said expression are shown to be in satisfactory agreement with results from experiments. Table 1; references 8 (Russian).

The Kinetic Characteristics of Chain Propagation and Transfer to Aluminum Alkyl During the High-Temperature Polymerization of Ethylene on Ziegler-Type Titanium-Magnesium Catalysts

[Article by A.A. Baulin and V.M. Kopylov; UDC 541(64+127):547.256]

[Abstract] The authors of the study reported herein conducted a series of experiments examining the kinetic characteristics of the process of high-temperature polymerization of ethylene on Ziegler-type titanium-magnesium catalysts. A bulk titanium-magnesium catalyst that was developed by the authors and that is designated TMK-1 was used in the experiments. TMK-1 contains 13.04% (by mass) Ti and is produced by reducing titanium tetrachloride with an ether solution of ethylmagnesiumbromide followed by high-temperature vacuum treatment. A second catalyst, designated TMK-2, was also used. TMK-2 ($TiCl_4$-$Mg(C_6H_5)_2$·$0.15MgCl_2$) differs from TMK-1 in that the former contains soluble components in the hydrocarbons. Both catalysts were activated by organoaluminum compounds in the polymerization stage. The ethylene was polymerized in a medium of n-heptane as the solvent on a metallic kinetic unit with a 0.3-1 reactor and with a screened electric mixer drive in accordance with a method detailed elsewhere. Radiochemical studies performed enabled the authors to determine (for the first time) the concentration of active growth centers and the rate constants of the elementary acts of the growth of the macrochain of polyethylene and the limitation of its growth by organoaluminum compounds during the polymerization of ethylene by dissolving the synthesized polyethylene in a hydrocarbon solvent at 433 K on titanium-magnesium catalysts as well as in a conventional Ziegler system based on titanium trichloride. The studies demonstrated that titanium-magnesium catalyst systems are characterized by a content of active centers that is severalfold higher than that of the conventional Ziegler system. The

studies further revealed that processes of high-temperature polymerization of ethylene involving the new titanium-magnesium catalysts are characterized by significantly higher chain growth rate constants than are processes in which a classical Ziegler system is used. The authors stated that the growth rate constants obtained for their new catalysts are supported by analogous results of a previously reported study of suspension polymerization of ethylene at 343 K and may be explained by the fact that the magnesium compound becomes a part of the composition of the polymerization complexes in the form of an active ligand that affects reactivity. Figures 2, table 1; references 21: 10 Russian, 11 Western.

Radical Polymerization of Monomers Capable of Association in Water

[Article by V.V. Yegorov, S.Yu. Zaytsev, and V.P. Zubov, Moscow State University imeni M.V. Lomonosov and Bioorganic Chemistry Institute imeni M.M. Shemyakin, USSR Academy of Sciences; UDC 541(515+64):542.952]

[Abstract] The creation of highly organized polymer systems having colloid-sized particles has attracted a great deal of interest in the past few years. The said systems, which are structurally similar to biological membranes, are important in two respects: as models of selected functions of such membranes and as materials and functional elements in molecular electronics, information technology, biotechnology, and medicine. These membrane-like polymers are generally produced by radical polymerization in associates of surface-active monomers. The authors of this review discuss the characteristic features of the radical polymerization of ionogenic surface-active monomers capable of forming associates in water and at a water-gas interface. The effect of the formation of fluctuation associates of monomer molecules on the rate of polymerization is demonstrated by way of the example of compounds with a low surface activity. Discussed next are the distinctive features of polymerization of the micelle-forming compounds in different types of micelles. The possibility of fixing associates of monomers by means of polymerization is demonstrated by way of the example of monolayer and polylayer formations of lipidlike compounds. In all of the systems examined, the authors trace the effect that the structure of the associates has on the kinetics of the said polymerization process. Specifically, they consider the effects of the method used to obtain the associates and the structure and concentration of the monomer. The universal dependence of the adjusted polymerization rate on the concentration of ionogenic monomer capable of association in water is established. The examples presented in this review clearly establish that polymerization makes it possible to fix associates of monomers and produce oriented polymer systems of colloidal

dimensions that are similar to various biological membranes (micelles, liposomes, and mono- and polylayers) that may eventually be used widely in various branches of sciences and technology. Figures 15, tables 4; references 77: 49 Russian, 28 Western.

The Effect of the Distinctive Features of the Structure of an Amorphous Phase on the Ferroelectric Characteristics of Copolymers of Vinylidene Fluoride and Tetrafluoroethylene

[Article by V.V. Kochervinskiy and V.G. Sokolov, Atomic Energy Institute imeni I.V. Kurchatov; UDC 541.64:539.2:547.321]

[Abstract] The authors of the study reported herein examined the ferroelectric characteristics of uniaxially stretched films of a copolymer of vinylidene fluoride with tetrafluoroethylene (in a 94:6 ratio). Isotropic films that were later texturized were prepared by precipitation from solutions in a mixture of DMPA and ethylacetate (method 1) or else by crystallization from a melt by hardening from 200° (method 2). The structure of the films produced and the process used to uniaxially stretch them were as described in another publication. For both types of films, the geometry during stretching was kept constant. The films' ferroelectric characteristics were studied by using a unit based on a Sawyer-Tauer circuit at a frequency of 50 Hz at ambient temperature. Their supermolecular structure was studied by using a unit with low-angle light scattering and with photographic recording of the scattering indicatrix. Their dielectric constant in weak fields was measured with an E7-8 bridge at a frequency of 1 kHz. The studies performed demonstrated that when all other conditions are equal, increasing the stretching temperature results in a decrease in residual polarization and the coercive field. Analysis of the structural characteristics of the films produced by both methods led the authors to conclude that two phenomena are important to development of the said phenomenon: the conformation makeup of the intercrystalline interlayerings and the values of the orientation functions for the chains of the crystalline and amorphous phases. Films produced by method 2 were found to form supermolecular structures in the form of optically anisotropic rods. Films produced from pure DMPA (method 3), on the other hand, were found to form spherolites with an average size of 2.6 μm. The electrophysical characteristics of the textured films were determined largely as a function of the structure of the isotropic films: The highest densities and highest degrees of crystallinity were found in films with the lowest dielectric constants. The enthalpies P_r and P_s obtained for a field of 1.26 MV/cm were found to increase regularly as the fraction of amorphous phase increased. Figures 6, tables 2; references 25: 12 Russian, 13 Western.

Anomalous Polymer Chain Relaxation Times in a Grafted Monolayer

[Article by A.M. Skvortsov, L.I. Klushin, and Yu.Ya. Gotlib, Leningrad Chemical and Pharmaceutical Institute and High Molecular Compounds Institute, USSR Academy of Sciences; UDC 541.64:539.199]

[Abstract] The authors of the study reported herein worked to develop a simple theory describing the laws governing the dynamic behavior of macromolecules in a monolayer and to discuss anomalous relaxation times based on concepts regarding the critical slowdown that occurs close to the "coil-elongated chain" phase transition point. By means of a mathematical analysis they demonstrated that for a chain in a monolayer, the molecular mass dependence of the time of large-scale motions in the direction perpendicular to the grafting plane has the form $\tau \approx N^3$. They further demonstrated that this form is maintained even when the grafting density and quality of the solvent chain change (as the solvent's quality diminishes, the relaxation time becomes increasingly dependent upon grafting density). They compared their derived relationships with the results of modeling monolayers by the Brownian dynamics method. As was hypothesized, the anomalous relaxation chain times observed in a monolayer were found to be linked to the critical slowdown close to the point of the "coil-elongated chain" transition. The equilibrium and dynamic behavior of short impurity chains disseminated into a monodisperse monolayer was also examined. The equilibrium characteristics of impurity chains in a monolayer were shown to be independent of the grafting density of the primary chains. Similarly, the relaxation times of impurity chains in a monolayer were shown not to be explicitly dependent on the said grafting density of the primary chains either. Figures 4; references 30: 11 Russian, 19 Western.

Dependence of the Process of the Formation of Interpolymer Complexes in Aqueous Solutions of Mixtures of Polyacrylic Acid and Copolymers of Vinyl Alcohol and Vinyl Acetate on the Molecular Parameters of the Components and Their Total Concentration

[Article by T.V. Budtova, N.G. Belnikevich, N.P. Ivanova, V.A. Kuznetsova, Ye.F. Panarin, Yu.N. Panov, A.Ya. Sorokin, and S.Ya. Frenkel, High Molecular Compounds Institute, USSR Academy of Sciences, and Plastopolimer Scientific Production Association, Okhotsk; UDC 541(64+49):532.77]

[Abstract] The authors of the study reported herein conducted a quantitative examination of the effect that

the molecular parameters of the components of polyvinyl alcohol and polyacrylic acid and the total polymer concentration have on the parameters of the interpolymer complex formed in an aqueous solution of the said mixture. Specifically, the following molecular parameters were considered: molecular mass, degree of esterification, and the type of distribution of the vinyl acetate links in the polyvinyl alcohol copolymers. Solutions of mixtures of polymers of the specified composition were prepared by quickly mixing two solutions of starting components taken in the appropriate proportions and were then subjected to intensive stirring. The polyacrylic acid specimens were obtained by polymerizing the monomer in benzene in the presence of a molecular mass regulator (isopropyl alcohol) and an initiator (dinitroazoisobutyric acid). The polymers were purified by reprecipitation from methanol into ethyl acetate. The copolymers of vinyl alcohol and vinyl acetate were synthesized from one and the same linear polyvinyl alcohol with an average degree of polymerization of 230 in accordance with a method detailed elsewhere. Seven copolymers were studied: PVS-10, SPL-10-B-3, SPL-10-B-10, SPL-10-B-14, SPL-10-S-9, SPL-10-S-14, and PVS-100. The adjusted relative viscosity in the range of the maximal deviation η_{rel} from the additive value, i.e., $\Delta\eta_{adj} = (\eta_{rel} - \eta_{rel}^{add})/\eta_{rel}^{add}$, was used as the measure of complex formation efficiency (this parameter is proportional to the effective volume of the complex). The mixture composition at which $\Delta\eta_{adj} = \Delta\eta_{rel}^{m}(c_m)$ was used as a second characteristic parameter. The analysis performed revealed that $\Delta\eta_{adj}$ increased as the total concentration of polymer increased and, beginning at a specified critical value, as the molecular mass of the components increased. This critical value was determined to be M = 4 x 10⁴ in the case of polyacrylic acid and M = 1.5 x 10³ for polyvinyl alcohol. The said pattern was interpreted from the standpoint of the formation of interchain hydrogen bonds resulting in the formation of a statistically branched supermacromolecule with trifunctional branching nodes. The study results were found to be in good agreement with models published previously by the authors themselves and with work published by others as well. Figures 5; references 13: 11 Russian, 2 Western.

Characteristic Features of the Polymerization of Propylene in Bulk on a Titanium-Magnesium Catalyst in the Presence of Hydrogen

[Article by A.M. Aladyshev, O.P. Isichenko, P.M. Nedorezova, V.I. Tsvetkova, Yu.A. Gavrilov, and F.S. Dyachkovskiy, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences; UDC 541.64:547.313.3]

[Abstract] The authors of the study reported herein examined the basic kinetic laws governing the polymerization of propylene in bulk and the properties of the polymers formed when titanium-magnesium catalysts were used in the presence of hydrogen. Other objectives of the study were to establish the reasons for deactivation of the titanium-magnesium catalysts during the course of the polymerization and to study the nature of the activating effect of hydrogen on the titanium-magnesium catalyst. Propylene was polymerized in a medium of rarefied monomer with the reactor completely full. A modified titanium-magnesium catalyst ($TiCl_4/MgCl_2$) containing 2.3% Ti combined with $AlEt_3$ was used. The titanium-magnesium catalyst was synthesized and provided by the Catalysis Institute of the Siberian Department of the USSR Academy of Sciences. The fractional composition of the polypropylene was determined by the method of successive extraction by cold and boiling n-heptane (in the last instance, for 16 hours), and the microstructure of specimens of isotactic polypropylene was determined by IR spectroscopy (using a Beckman-4260 spectrometer). The structure of a chain of atactic polypropylene was determined by the ^{13}C NMR method (using a Bruker-HM-400 spectrometer). The granulometric composition of the polypropylene was determined by fractionation on a standard set of molecular sieves in a propyl alcohol medium. The studies performed revealed that adding even small amounts of hydrogen (up to 5 x 10⁻³ mol/l) to the reaction medium results in an increase in catalytic activity in the study system by a factor of 3 to 5. Increasing the concentration of hydrogen in the reaction mixture was found to result in somewhat of a decrease in the isotacticity of the polypropylene formed and, consequently, in an increase in the amount of atactic fraction. Conducting the polymerization of propylene in bulk on a titanium-magnesium catalyst in the presence of hydrogen was also found to facilitate an increase in the granular weight (density) of the polymer particles formed. The non-steady-state nature of the polymerization of propylene in bulk in the presence of hydrogen was demonstrated to be linked to the occurrence of reactions of bimolecular destruction of the active centers. The observed decrease in the activity of the catalysts system during the polymerization of polypropylene was determined to be linked to processes occurring between the components of the catalyst itself. When all other conditions remained equal, increasing the polymerization temperature resulted in a change in the stereoregular composition of the polypropylene formed. The maximum degree of isotacticity was observed for polypropylene produced at temperatures between 70 and 80°C. Increasing the polymerization temperature was also found to result in an increase in those parameters characterizing the steroregularity of the isotactic fraction. The stereoregular composition of the atactic fractions for both systems studied were found to be virtually identical, thus leading the authors to conclude that the non-stereospecific active centers of the study titanium-magnesium catalyst and microspherical δ-$TiCl_3$ are quite similar in nature. Figures 4, tables 3; references 14: 6 Russian, 8 Western.

Modifications of Viscose Fibers as a Method of Reducing the Combustibility of Polymer Composites

[Article by S.Ye. Artemenko, L.G. Panova, V.I. Besshaposhnikova, and N.A. Khalturinskiy, Saratov Polytechnic Institute; UDC 541.64:547.458.81]

[Abstract] The authors of the study reported herein examined the feasibility of modification of viscose fibers as a method of reducing the combustibility of polymer composites. As a polymer binder, they used SF-342A aniline phenolformaldehyde resin (GOST 13694-80) and MSR-100S (TU 6-05-1867-79) melamine formaldehyde resin. The polymer composites were synthesized by the method of compression pressing at 425 +/- 5 K under a pressure of 10 to 12 MPa for a period of 3 minutes per millimeter of the specimen thickness followed by heat treatment at the forming temperature for 2 hours. The fibers were modified by the method of impregnation of the fibrous canvas or thread with an aqueous solution of different concentrations of antipyrenes followed by drying until a constant weight was achieved. The specimens were subjected to x-ray structural studies on a Dron-3 diffractometer. The reaction of the antipyrene with the fiber was studied by the method of IR spectroscopy on a Specord IR-75 with a MIR-4 attachment. The heat resistance and thermolysis of the specimens was studied by thermogravimetric analysis on a Derivatograph Q-1500 D. Specimens weighing 0.2 g were heated in air to a temperature of 1,000°C at a constant heating rate of 10 K/min. The studies performed indicated that phosphorus-containing antipyrene is indeed effective in reducing the combustibility of polymer composites. Polyphosphate was demonstrated to act as an antipyrene and filler that transformed highly combustible polymer composites into hard-to-burn materials. Data from staged gas pyrolytic chromatography studies performed indicated that the antipyrenes studied changed the composition of the pyrolysis gases: The yield of water increased by a factor of 2.3, and the yield of carbon dioxide increased by a factor of 1.5 when compared with the gas yields from the untreated viscose fiber. The effect of heat-resistant antipyrene on the mechanism of the fiber's decomposition was found to be linked with hydration of the sodium polyphosphates in an aqueous medium and with its transition into a hexahydrate. In summary, polyphosphate was demonstrated to act as an antipyrene and filler that transformed highly combustible polymer composites into hard-to-burn materials. More specifically, in its hydrated form, polyphosphate penetrates inside the volume of the viscose fibers, reacts with them by forming hydrogen bonds, and inhibits the combustion of the treated viscose fibers both in the condensed and gas phases. The studies thus confirmed that polyphosphate may be added to polymer composites in the form of modified fibers in amounts up to 20% (by mass). In the said amounts, the polyphosphate has the effect of increasing the modified polymer composite's flexural strength by 15 to 30% and its tensile strength by 15 to 20%. Figures 6, tables 3; references 6 (Russian).

Effect of the Simultaneous Action of External Force Fields on Molecular Mobility in Polymers

[Article by A.V. Potemkin and Yu.V. Zelenev, Moscow Textile Institute imeni A.N. Kosygin; UDC 541.64:539.199]

[Abstract] The authors of the study reported herein developed a quantitative description of the processes of molecular mobility occurring in polymers subjected to the simultaneous effect of different force fields. The description was developed by means of the method of nonequilbirum thermodynamics. During the course of their analysis, the authors considered the effect of changes in the height of potential barriers as a result of the interaction of kinetic units of the given subsystem with the external force fields. The results of computations performed by using mathematical relationships derived were compared with the results of experiments performed for polymethyl methacrylate at a temperature of 313 K and a field strength of 7,000 Oe. The maximum relative error amounted to about 10%, thus leading the authors to conclude that their proposed theory was adequate. The authors analysis led them to conclude that a high-frequency periodic field will affect a polymer system in the same manner as a constant field with an amplitude equal to A_0 times the square root of $K'/2K_0$. A low-frequency periodic field, on the other hand, will facilitate a change in the dielectric characteristics of the material during the relaxation process (these characteristics will depend on the amplitude of the field and the moment in time, i.e., t_0, at which relaxation is measured). Figures 2; references 7 (Russian).

Study of Molecular and Supermolecular Structural Changes in Sodium Pentadecylsulfonate-Polyethyleneglycol-Water System as Function of Molecular Mass of Polymer

[Article by L. M. Garibyan, A. G. Sarkisyan, V. G. Barkhudaryan and R. S. Oganesyan, Yerevan Medical Institute; UDC 541.182.02:541.64]

[Abstract] Effect of polyethyleneglycol with molecular mass of 2000, 6000, 20,000 and 40,000 with a ratio of sodium pentadecylsulfonate/polyethyleneglycol [SPDS] with ratio of 8/2, 6/4 and 4/6 on the structure of the laminar phase of an SPDS + water system which served as a model of biological membranes. Polyethyleneglycol with molecular mass of 2000, 20,000 or 40,000 did not

affect molecular packing of the SPDS-water liquid crystal system but changed the supermolecular formations differently. Polyethyleneglycol with molecular mass of 6000 stabilized the system, screened the entry of water between the layers and changed the supermolecular formations accordingly. Figures 4; references 1 (Russian).

Heteroorganic Metal-Containing Paramagnetic and Ferromagnetic Polymers. Part 3. Magnetic Properties of Products From Thermal Condensation of Polymetalloorganosiloxanes

[Article by A.A. Zhdanov, A.L. Buchachenko, A.Yu. Dyakonov, O.I. Shchegolikhina and M.M. Levitskiy, Institutes of Heteroorganic Compounds, of Chemical Physics, and of Petrochemical Synthesis, USSR Academy of Sciences, Moscow; UDC 541.67:538.222:541.64:547.1'13:547.1'128]

[Abstract] An analysis was conducted on the magnetic properties of pyrolytic (550-800°C for 10-120 min under Ar) products of paramagnetic polymetalloorganosiloxanes containing either Fe, Co or Fe and Co. The resultant products were shown to be ferromagnetic due to reduction of Fe, with the intensity of magnetization directly related to the Si/M ratio (M = metal). Magnetization was greater for mixed polymers with Fe and Co since Co served to catalyze reduction of Fe. Figures 3; tables 2; references 3 (Russian).

Inhibition of Vinyl Monomer Polymerization by Sulfur-Containing Hydroquinolines

[Article by O.A. Ozhogina, M.D. Goldfeyn, N.B. Chumayevskiy, Kh.S. Shikhaliyev, Zh.V. Shmyreva and E.G. Rozantsev, Institute of Chemical Physics imeni N.N. Semenov, USSR Academy of Sciences, Moscow; UDC 541.127:542.943.8:547.831.3:541.64:541.515]

[Abstract] Seven dihydro-4,4-dimethyl-1H-3,2-dithiolo[5,4-c]quinoline-1-thiones (I) and gossypol were tested for inhibition of vinyl polymerization in their capacity as antioxidants. Kinetic studies on inhibition of polymerization of styrene, methyl methacrylate and acrylic acid demonstrated that hydroqinolines lacking a sulfur-containing ring were far less effective as inhibitors. Accordingly, inhibition by the thiones was attributed to reaction of the $RO_2\cdot$ radical with the S atom, leading to the formation of an intermediate and eventual removal of an H atom from the NH group. Stoichiometric coefficients of the hydroquinolines ranged from 0.30 to 2.4. Studies on gossypol-mediated inhibition yielded a stoichiometric coefficient of almost 3.4 and a 4-fold lower critical concentration for the inhibitor than for the hydroquinones. Figures 5; tables 1; references 5: 4 Russian, 1 Western.

Release of Gaseous Acceptors of Peroxyl Radicals by Polymeric Materials

[Article by V.A. Belyakov, R.F. Vasilyev and G.F. Fedorova, Institute of Chemical Physics imeni N. N. Semenov, USSR Academy of Sciences, Moscow; UDC 535.379:541.127:542.943:547.631.2:541.515]

[Abstract] Chemiluminescence studies on a series of polymers revealed release of a gaseous entity reacting with peroxyl radicals (HROO) and inhibiting oxidation. Washed samples of polypropylene, polyethylene and polymethyl methacrylate are low emitters, while siloxane and black rubber are high emitters. Release is increased by pyrolysis of the samples, with the concentration of the relased reactant reaching levels of 10E-8 to 10E-7 M. Since the reaction rate with peroxyl radicals is on the order of $1.5 \times 10E+8\ M^{-1}sec^{-1}$, i.e., approaches that of diffusion-limited reactions, the reactant may well be a radical. Figures 1; references 3 (Russian).

Effect of Aluminum Content of Aluminum Silicate on Preparation of Hydrogen by Radiocatalytic Decomposition of Water

[Article by A.A. Garibov, T.N. Agayev and R.D. Kasumov, Radiation Research Section, Azerbaijan SSR Academy of Sciences; UDC 541.14:543.422]

[Abstract] Comparative kinetic studies were conducted on production of hydrogen by radiocatalytic decomposition of water at 300 K and 9.43 Gy/sec γ-irradiation. Hydrogen production per 100 eV increased ca. 2.5-fold to a plateau as [Al] rose from 0 to ca. 10%, failing to increase further as [Al] increased to 67%. The latter observations indicated that only a certain fraction of the Al component is involved in active radiocatalytic centers active in the radiolysis of water. At 723 K hydrogen production plateau was reached with an [Al] of ca. 35%. Accordingly, the data were interpreted to demonstrate that Al^{3+} species, representing a small fraction of total Al in the silicate, act as the active centers for adsorption of water and are responsible for energy transfer from the catalyst to the water molecules. The net effect is deformation of the water molecules which leads to their decomposition and release of hydrogen. Figures 3; tables 1; references 15: 12 Russian, 3 Western.

Impact of Accelerated Electron Pulses on Radiochemical Processes in Linear Polyadducts of Aromatic Diamines and Diepoxides

[Article by A.S. Kolotilkin, V.A. Tkachev, Ye.I. Maltsev, A.Yu. KRYUKOV AND A.V. Vannikov, Institute of Electrochemistry imeni A.N. Frumkin, USSR Academy of Sciences; UDC 541.15]

[Abstract] Impact of accelerated electrons (4 MeV electrons; 900 Gy dose/pulse) on polyadduct of N,N'-dibenzyl-4,4'-diaminodiphenylmethane and 2,2-bis(4-[2,3-epoxypropoxy]phenyl)propane with and without 10% CBr_4 was shown to produce a number of short-lived (τ < 50 msec) fragments. The 60 μm-thick samples of the 11,000 MW adduct yielded three major radiolytic fragments, which were identified from peak absorption bands at 450, 490 and 580 nm. The latter two were attributed to cation radicals, while the nature of the 450 nm product remains enigmatic. In addition, a secondary product with τ > 100 msec and a broad adsorption band increasing in intensity was observed at 380 nm. The latter product was attributed to protonation of an amino group formed under direct action by the electrons, leading to formation of an quinone-imine structure. In the presence of CBr_4 lifetimes of the primary fragments were prolonged to 1 msec, although the 380 nm fragment was not detected. In general, the data were consistent with the formation (2.0 sec^{-1}) of an analog of Michler's hydrol as the final product. Figures 2; tables 1; references 11: 9 Russian, 2 Western.

ESR Studies on Initiation of Tetrafluoroethylene (TFE) Polymerization by Irradiated Perfluoropelargonic Acid (PFPA)

[Article by S.R. Allayarov, D.A. Gordon, I.P. Kim, F.A. Baybikov and I.M. Barkalov, Institute of Chemical Physics imeni N.N. Semenov, USSR Academy of Sciences; UDC 541.14]

[Abstract] ESR measurements were used to monitor low temperature (77 K) formation of paramagnetic centers in the course of γ-irradiation of PFPA and their fate on heating to room temperature (300 K). Radiolysis was shown to lead to formation of paramagnetic centers with overlapping spectra in a yield of 0.05 G/eV. Heating led to disappearance of all but two centers at Tg = 207 K. The data were consistent with a mechanism of TFE polymerization initiated by active centers stabilized on PFPA since ESR spectra during polymerization remained constant. Figures 2; references 2: 1 Russian, 1 Western.

Distinctive Features of the Morphology of Microdiamonds and the Content of Sodium Impurities in Garnets and Potassium in Pyroxenes of Two Xenolites of Eclogites From the Udachnaya Kimberlite Tube in Yakutiya

[Article by N.V. Sobolev, academician, I.T. Bakumenko, E.S. Yefimova, and N.P. Pokhilenko, Mineralogy and Petrography Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk; UDC 552.8:549.21:571.56]

[Abstract] In addition to containing diamonds greater than 0.5 mm in size that may be detected by visual observation, kimberlites and deep xenolites also contain smaller diamonds (<0.5 mm in size) that are conventionally termed microdiamonds. These microdiamonds may be overlooked when deep xenolites are studied if special consideration is not given to the indirect mineralogic evidence of their presence. In an effort to increase the amounts of microdiamonds recovered from xenolites, a study was conducted to identify the characteristic features of the morphology of microdiamonds contained in individual xenolites of the Udachnaya kimberlite tube in Yakutiya. Specimens of rocks from the tube were subjected to thermochemical decomposition at the Central Geological Prospecting Scientific Research Institute [TsNIGRI] in order to verify the possibility of their containing microdiamonds. The basis for this verification was the detection of a stable sodium impurity in the garnets and potassium in the pyroxenes of a number of xenolites, which in turn is an indication that the rocks were formed in a region in which diamond is stable. Very small diamond crystals (ranging in size from 30 to 500 µm) were found in the insoluble residue of two specimens. Separate decomposition of the garnet and pyroxene fractions demonstrated that diamond microinclusions were present only in the pyroxene grains. The morphology of the diamonds discovered was then studied by means of a JSN-35 scanning electron microscope. The studies performed indicated that the potential diamond content of eclogites containing elevated quantities of Na$_2$O impurities in their garnets and elevated quantities of K$_2$O in their respective pyroxenes is indeed an indication of the presence of microdiamonds that cannot be identified visually. The said microdiamonds exist in a broad morphological series ranging from octahedral to pseudo-cubic crystals (the fact that the latter are much larger than the former was interpreted as confirmation of the growth nature of the formation of the microdiamonds' faces). Overall, the pyroxenes of the diamond-bearing eclogites examined contain smaller amounts of potassium impurities than do pyroxenes from diamonds. This was taken as a confirmation of the previously published hypothesis regarding the extraction of potassium from pyroxenes during recrystallization under conditions of a subsolidus at reduced pressures. The fact that the elevated content of potassium impurities in the pyroxenes of the study specimens remained at the level of average values for inclusions in diamonds was interpreted as confirming the fact that these rocks had been subjected to recrystallization at higher pressures than are typical for diamond-bearing eclogites. The different behavior of the xenolites of especially deep eclogites in the subsolidus region (i.e., recrystallization with a loss of most of the potassium or with preservation of it as such) was seen as confirming 1) the complexity of the mechanism of the transport of deep xenolites by kimberlite and 2) their complexity in the subsolidus region at different pressures. Finally, the researchers concluded that only a combined change in the Na$_2$O content in garnets and in the K$_2$O content in the respective pyroxenes may be used for barometric estimates owing to the differences in recrystallization conditions and primary K$_2$O contents. Figures 2, tables 3; references 15: 11 Russian, 4 Western.

Experimental and Thermodynamic Modeling of a C-O-H Fluid in Equilibrium With Graphite and Diamond Given High *PT*-Parameters

[Article by I.I. Fedorov, A.I. Chepurov, N.Yu. Osorgin, A.G. Sokol, and Academician N.V. Sobolev, Mineralogy and Petrography Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk;UDC (536.45+539.893):(546.26.126+542.7)]

[Abstract] The fluid conditions existing in a C-O-H system are generally modeled by thermodynamic calculations under the assumption that the fluid consists of H$_2$O, H$_2$, CO, CO$_2$, OH$_4$, and O$_2$. Only one published work is known to contain calculations for pressure-temperature parameters close to the crystallization conditions of kimberlite diamonds. In view of this fact, the authors of the study reported herein conducted theoretical and experimental examinations of the gaseous phase in the system C-O-H under atmospheric and high pressures and have calculated the composition of the said fluid given P-T-f$_{O2}$ values corresponding to the crystallization parameters of natural diamonds. The thermodynamic characteristics of the study fluid (assumed to be an ideal mixture of real gases) were based primarily on data published by Barin and Knacke in 1973. The experimental studies of the system C-O-H were performed on a multiple-punch high-pressure device. Sealed platinum ampules holding weighed specimens of graphite or anthracene and water were used to study the reaction of anthracene with hydrogen in accordance with an experimental methodology described elsewhere. The hydrogen source (TiH$_{1.9}$) was located outside the ampules holding the anthracene. The experiments were conducted for 30 minutes, after which the specimens were quenched to room temperature at a rate of 150 to 200 °/s or by slow cooling without alleviating the pressure. The ampules were then cooled with liquid nitrogen,

after which their contents were subjected to chromatographic analysis in a helium atmosphere heated to 150-200°C. Both the experimental and calculated data confirmed that the main components of C-O-H fluid in equilibrium with solid carbon given high pressure and temperature parameters are H_2O, CH_4, H_2, and CO_2. The acetylene established during the analysis was in the form of carbon molecules adsorbed on the surface; only negligible amounts of acetylene were present in the fluid. Chromatographic analysis showed an elevated water content relative to the hydrocarbons as compared with what was predicted by the theoretical calculations. This was attributed to diffusion of hydrogen from the ampule under the high pressures and temperatures used as well as to a partial loss of gaseous phase when the ampule was unsealed. Slow cooling resulted in the formation of heavy hydrocarbons. It was hypothesized that they were a part of the high-temperature fluid in the oxygen-free system C-H or else were formed when the specimens were quenched. A sharp increase in C_3H_6 content was observed to occur at high temperatures. The speculation was that it is linked to errors in its thermodynamic constants. The studies performed thus demonstrated that the composition of gases adsorbed on the surface of solid carbon is very different from that of the gaseous phase in equilibrium with it. It was further concluded that the compositions of the volatile components determined in natural diamonds do not reflect the fluid conditions of diamond formation. This finding was speculated to be linked with the postcrystallization changes in the composition of the captured gases. The heavy hydrocarbons established in the satellite minerals of diamond were concluded to form as the specimens cool but to not become a component of the high-temperature fluid. The authors concluded by stating that their results confirm previously published ideas regarding the important role of hydrogen or juvenile hydrocarbons in the diamond formation process and the hypothesis that methane oxidation reactions resulting in the release of free carbon and water are the source of carbon for diamond and graphite. Figure 1, table 1; references 15: 9 Russian, 6 Western.

New Types of Silver Deposits in the Dukat Ore-Bearing Region of Northeast USSR

[Article by A.I. Kalinin and V.Ye. Natalenko, North Eastern Affiliate, Central Scientific Research Geological Prospecting Institute of Nonferrous and Noble Metals, Magadan; UDC 553.41.078.2(571.65)]

[Abstract] The Dukat ore-bearing region, which is a part of the Yana-Kholmsk fold system, is known to contain veined low-sulfide silver and disseminated and disseminated-streaked tin-and-sulfur deposits as well as sulfide and silver-and-polymetal deposits. It is likely that additional types of silver deposits are also present in the Dukat region. This hypothesis is based on (among other things) the age of the mineralization in the area. All known silver-bearing ore bodies of the Dukat deposit and Omsukchan metallogenetic zone date from the Late Cretaceous-Paleogene period, as is the case with the Okhotsk-Chukot belt of volcanic origin. The silver deposits of a representative segment of the Dukat ore field, namely, the ore field bearing the same name, dates from more than one time period. Studying the conditions of the localization of the region's silver deposits, their ore formation links, and their geological history will make it possible to predict new genetic, formation, and structuromorphological types of deposits. The presence in the Dukat ore region of stratiform sedimentary silver deposits in deposits of the Omsukchan series is highly likely in view of the fact that the main geological prerequisites for such formations are temporal (and often spatial as well) proximity to Early Cretaceous ore genesis and continental sediment accumulation under lake and swamp conditions. The fundamental possibility of the formation of syngenetic sedimentary silver deposits has been confirmed by the discovery of deposits at Waterloo and in California and Mexico. All of the characteristic indications of such deposits (including the specialization of ore fields of metal origin, the characteristic association of the latter with tin and polymetals, the formation of endogenous mineralization in lake and swamp basins, and the presence of carboniferous matter) are present in the area. The search for a new type of silver formation in the Dukat ore field should begin with explorations in the root bed of rich quartz-carbonate viens that have to date been found only in the form of fragmented ore deposits. The most likely method of finding the desired ore bodies and beds is to analyze the Early Cretaceous structures. All existing data indicate that they will be in the form of cross veins localized in formations of the Askoldin complex, the lowermost strata of the Omsukchan series, and in the foundation of the rock of volcanic origin. Detailed structural studies conducted in reference ore fields have made it possible to estimate the role of the new structuromorphological types of deposits and ore bodies. The said studies have indicated that the new deposits will likely be tube and screened formations as well as stockwork mineralization in the foundation of the Cretaceous formations exposed in individual ore fields. The only tube ore-bearing bodies detected to date have been along the northern edge of the Dukat ore region during explorations in the Nachalnyy section. Signs of such deposits have been detected in other areas as well, however. The authors of this article detail the morphological features and local laws governing the location of such deposits by way of the example of the ore tubes of the Nachalnyy section of the Dukat ore field, where two types of ore-bearing tubes have been found. Each tube has a cross-sectional area of about 300 m^2, a virtually plumb drop, and a length up to 350 m. Figures 3; references 9: 8 Russian, 1 Western.

Age of the Gold-Bearing Conglomerates of the Zaaltayskaya Gobi (Mongolia)

[Article by V.F. Shuvalov, Ye.V. Devyatkin, and T. Semeykhan, Soviet-Mongolian Geological Expedition, USSR Academy of Sciences and Mongolian People's Republic Academy of Sciences, Moscow, Lake Science Institute, USSR Academy of Sciences, Leningrad, Geology Institute, USSR Academy of Sciences, Moscow, and Geology Institute, Ulan-Bator, Mongolia; UDC 551.763.3]

[Abstract] The Zaaltayskaya Gobi, located in the southwestern portion of Mongolia, is one of the least accessible and least studied regions of Central Asia. Prospectors have recovered placer gold from the Zaaltayskaya Gobi since the end of the last century and beginning of the present century. Explorations of the area in the regions of the Ongon-Ulan-Ula, Altan-Ula, and Nemegetu ridges have confirmed that most of the gold is located in reddish nodular conglomerates that are confined to the periphery of mountainous elevations with metamorphosed Paleozoic formations at their center. Gold has also been found in gray channel and terrace sediments developed in "dry" valleys of temporary streams cutting through the Altan-Ula and Nemegetu. The fact that these sediments date to the Quarternary Period is undisputed. The age of the conglomerates had been open to debate. There had been speculation (in a 1977 publication) that the conglomerates were formed in the Neogene or Early Quarternary periods. The gold-bearing conglomerates have been the subject of additional studies (in 1983 and 1987-1989). According to the latter, the gold-bearing red conglomerates represent the bottommost (basal) level of a rather large (up to 150 m) mass mottled with conglomerates, sandstones, gravelites, argillites, and clays of various origins. The basal conglomerates are located in a seam ranging from 2-3 to 12-15 m in thickness. The seam in which the gold-bearing conglomerates are present consists of three bands of differing structure and color. The authors of this article have detailed the structure of the said bands layer by layer from the bottom up. On the basis of the data presented, the authors conclude that the gold-bearing red conglomerates of the Altan-Ula and Nemegetu region are located in the bottommost layers of the upper Cretaceous layer and the base of the Bainshirein suite and that they most likely date to the Senoman stage. The placer gold deposits in the Upper Cretaceous sediments of the Zaaltayskaya Gobi form an area stretching nearly 400 km in an east-west direction. The formation of the placer deposits may be linked to the erosion of the local crust by wind in the pre-Upper Cretaceous period. The studies performed provide a basis for demarcating a new large placer gold province extending more than 1,500 km from east to west from the Zaaltayskaya Gobi to Yuzhnyy Altay. Figure 1; references 14 (Russian).

Native Gold of Ruby-Bearing Marbles of Regional Metamorphic Complexes of the Ural Area and Its Role in the Formation of Placer Deposits

[Article by V.V. Murzin, A.Yu. Kisin, and V.N. Sazonov; UDC 549.283:553.824(470.5)]

[Abstract] The authors of the study reported herein examined the marbles developed within the confines of the Murzinsk-Aduy, Kochkar, and other metamorphic complexes of the Eastern Ural uplift. In recent years, these marbles have been found to contain native and placer corundums, including rubies, and their formation has been linked with processes of progressive and regressive stages of metamorphism. The Kochkar metamorphic complex is known to contain numerous gold-bearing placer deposits. In the overwhelming majority of cases, these deposits are found in the aforesaid marbles. The geological and exploratory studies on the faceting corundum that are reported herein establish that the transfer of the matter of the placer deposits was very insignificant and that it was accumulated instead in conjunction with processes of karst formation. The placer gold deposits and ruby deposits have been shown to be confined to the same space, and the washings containing elevated amounts of placer gold and ruby have shown a tendency to be located in narrow linear zones conforming to the expanse of the marble. Overall, the studies performed established the association of the native gold and rubies in the native deposit. Particles of native gold have been found in millings weighing 1 to 3 kg and in insoluble residues weighting 100 to 200 g of marble samples from the Kochkar and Murzinsk-Aduy complexes. The marbles contain scatterings of graphite, apatite, ruby, and pyrite (octahedra and icosahedra). Its cracks include isolated sphenes, pargasite, diopside, ruby, pyrite (cubes and pentagondodecahedra), pyrrhotine, phlogopite, and chlorite. The incidence of gold in the millings and insoluble residues of the marble samples ranged from 1 to 20, with most of the gold being found in those segments of the marble that had an elevated pyrrhotine content. The gold particles ranged from 20 to 150 µm in size, with 40 to 60 µm being the most commonly encountered size range. Chemical analysis of the gold found did not reveal any explicit relationships between the composition of the gold particles and their size or morphology. The most characteristic feature of the composition of the gold found was its anomalously high grade (970 or higher in 13 of the 16 grains analyzed). The marbles and their accessory mineral deposits were found to have been formed during various periods of regional metamorphism. Magnesial-calcite marble with scattered mineral deposits (ruby, graphite, apatite, and pyrite octahedra and icosahedra) were found to have formed in the progressive stage. The formation of mineralized cracks in both types of marbles encountered was linked to the beginning of the pneuma-tolytic-hydrothermal stage. These cracks were shown to contain unevenly colored corundum, phlogopite, tourmaline, sphenes, and rutile, as well as other minerals. In

the regressive stage of metamorphism, the marbles were subjected to the effect of metamorphic thermal springs carrying gold, silver, lead, zinc, and arsenic and forming ore formations that were richest in gold and silver (the Andreyev deposit). The gold formed in the progressive stage of metamorphosis was found to be of the highest quality (in the sense that it was pure of silver). This gold, while not formed in large agglomerates, had nevertheless been shown to be one of the sources of the mineral concentrated in the tracer deposits in the study area. Figure 1, table 1; references 4 (Russian).

Stability and Electro-Surface Properties of Aqueous Dispersions of Oxidized Synthetic Diamond

[Article by V. N. Moraru, F. D. Ovcharenko and L. A. Totskaya, Department of Natural Dispersed Systems, Physico-chemical Institute imeni A. V. Bogatskiy; UkSSR Academy of Sciences, Kiev; UDC 541. 18.046.7:621.921.34]

[Abstract] A study of the stability and electro-surface properties of aqueous dispersions of oxidized synthetic diamond in a wide interval of concentrations of KCl, $BaCl_2$, YCl_3 and pH of the medium of 2.4-12.0 was performed to explain the nature of aggregative stability of aqueous dispersions of oxidized synthetic diamond and the role of different mechanisms in ensuring their stability. The data indicated the existence of particles of a hydrate boundary layer on the surface of the particles. In the acid region of the pH with KCl concentrations near to the coagulation threshold, aggregation stability of disperions was ensured by structural forces of repulsion. The electrostatic factor played the predomiant role in neutral and alkaline regions of pH. Experimental data obtained agreed quantitatively closely with the DLVO theory. Figures 4; references 11: 6 Russian 5 Western.

SUBSCRIPTION/PROCUREMENT INFORMATION